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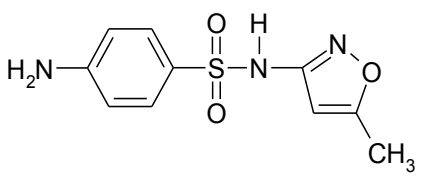
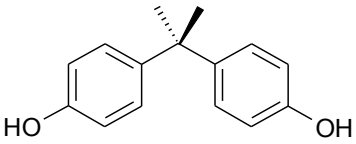
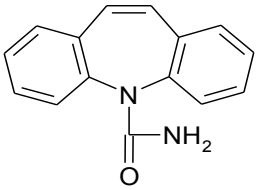
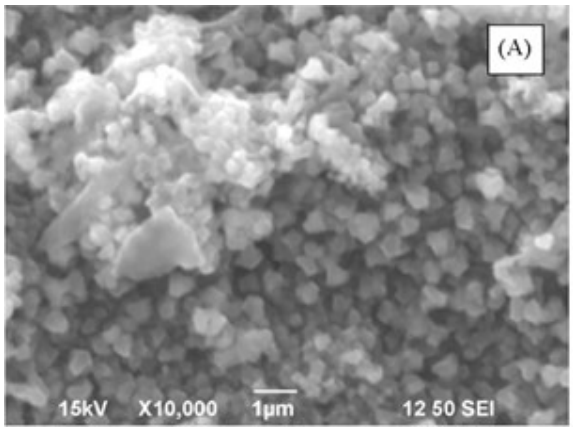
The Impact of Membrane Fouling on the Removal of Trace Organic Contaminants from Wastewater by Nanofiltration

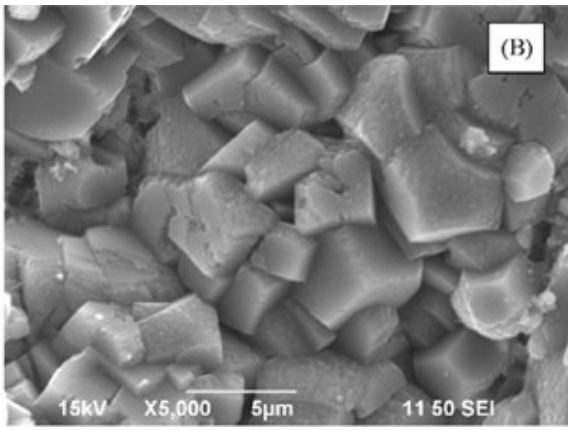
Dirk Vogel











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Summary/Abstract

Nanofiltration (NF) is an attractive option for the treatment of wastewater e.g. municipal wastewater and landfill leachate. However, membrane fouling can be a major obstacle in the implementation of this technology. Fouling of nanofiltration membranes by humic acids (HA) was investigated using bisphenol A (BPA) as an indicator chemical to differentiate between various mechanisms that may lead to a change in solute rejection. Three commercially available NF membranes were investigated and an accelerated fouling condition was achieved with a foulant mixture containing humic acids in an electrolyte matrix. The effects of membrane fouling on the rejection of BPA were interpreted with respect to the membrane pore sizes and the fouling characteristics. Results reported here indicate that calcium concentration in the feed solution could be a major factor governing the humic acid fouling process. Moreover, a critical concentration of calcium in the feed solution was observed, at which membrane fouling was most severe. Membrane fouling characteristics were observed by their influence on BPA rejection. Such influence could result in either an increase or decrease in rejection of BPA by the three different membranes depending on the rejection mechanisms involved. It is hypothesised that these mechanisms could occur simultaneously and that the effects of each might not be easily distinguished. However, it was observed that their relative contribution was largely dependent upon membrane pore size. Pore blocking, which resulted in a considerable improvement in rejection, was prominent for the more open pore size TFC-SR2 membrane. In contrast, the cake-enhanced concentration polarisation (CECP) effect was more severe for the tighter NF270 and NF90 membranes. For hydrophobic solutes such as BPA, the formation of the fouling layer could also interfere with the solute-membrane interaction, and therefore, exert considerable influence on the separation process.

The combined impact of humic acid fouling and $CaCO_3$ scaling on the rejection of trace organic contaminants by a commercially available nanofiltration membrane was investigated in this study. Due to the presence of humic acid in the feed solution, $CaCO_3$ scaling behaviour differed substantially from that of a pure $CaCO_3$ solution. A prolonged induction period was consistently observed prior to the onset of membrane scaling. In addition, membrane scaling following humic acid fouling did not result in a complete loss of permeate flux. This is consistent with the absence of any large $CaCO_3$ crystals. In fact, the $CaCO_3$ crystals on the membrane surface were quite small and similar in size, which would result in a relatively porous cake layer. At the onset of $CaCO_3$ scaling the rejection of all

three trace organic contaminants started to decrease dramatically. The observed decrease in rejection of the trace organic contaminants was much more severe than that reported previously with a single layer of either organic or colloidal fouling. Such severe decrease in rejection can be attributed to the extended cake-enhanced concentration polarisation effect occurring as a result of the combination of membrane fouling and scaling. The porous $CaCO_3$ scaling layer could lead to a substantial cake-enhanced concentration polarisation effect. In addition, the top $CaCO_3$ scaling layer could reduce the wall shear rate within the underlying humic acid fouling layer, causing an additional concentration polarisation (CP) effect.

Keywords: Nanofiltration, Membrane fouling, Membrane scaling, Trace organic contaminants, Cake-enhanced concentration polarisation, Bisphenol A

Table of Contents

List of figures

List of tables

Glossary

ACN	Acetonitrile
AFM	Atomic force microscope
AOM	Algogenic organic matter
BDIM	Bromodiiodomethane
CA	Cellulose acetate
CCFs	Caustic cleaning formulations
CBZ	Carbamazepine
CECP	Cake-enhanced concentration polarisation
CN	Cellulose nitrate
CP	Concentration polarisation
CTA	Cellulose triacetate
DHAN	Dihaloacetonitrile
DI	Deionised
DIC	Diclophenac
DBPs	Disinfection by-products
DOC	Dissolved organic carbon
EfOM	Effluent organic matter
HA	Humic acid
HAA	Haloacetic acids
HPLC	High-performance liquid chromatography
HpoA	Hydrophobic acid organic matter
IBU	Ibupropen
ICs	Industrial chemicals
IS	Ionic strength
I-THMs	Iodinated trihalomethanes
LPRO	Low pressure reverse osmosis
MBR	Membrane bioreactor
MF	Microfiltration
ML	Molecular length
MW	Molecular weight
MPA	Minimum projection area
MWCO	Molecular weight cut-off

NDBA	N-nitrosodi-n-butylamine
NDMA	N-Nitrosodimethylamine
NDPA	N-nitrosodipropylamine
NF	Nanofiltration
NOM	Natural organic matter
NPX	Naproxen
PA	Polyamide
PAN	Polyacrylonitrile
PC	Polycarbonate
PCPs	Personal care products
PEIs	Polyetherimides
PESs	Polyethersulfones
PhACs	Pharmaceutically active compounds
PI	Polyimide
PFC	Perfluorinated organic compounds
POPs	Persistent organic pollutants
PP	Polypropylene
PPCPs	Pharmaceutical and personal care products
PSU	Polysulfone
PTPs	Pesticide transformation products
PVA	Polyvinyl alcohol
PVDF	Polyvinylidenefluoride
RO	Reverse osmosis
SEM-EDS	Scanning electron microscope-electron dispersive spectroscopy
SHs	Steroid hormones
SMX	Sulfamethoxazole
TCS	Triclosan
TFC	Thin-film composite
THM	Trihalomethane
TIM	Triiodomethane
TMF	Trans membrane flux
TMP	Trans membrane pressure
TOC	Total organic carbon
TrOCs	Trace organic compounds

UF	Ultrafiltration
UV	Ultraviolet
WWTP	Wastewater treatment plant

1 Introduction

Chapter 1 of this work gives a general introduction into filtration using nanofiltration/reverse osmosis (NF/RO) membranes including fundamentals, transport and separation mechanisms, (commercial) applications as well as some insight into the classification, structure, and materials of NF/RO membranes. Furthermore, a comprehensive look is taken at the removal of trace organic contaminants (TrOCs) by NF/RO, a highly complex matter affected by characteristics of the membrane, the feed solution, the solutes, and the operational conditions of the NF/RO filtration process. Additionally, it is focussed on the implications of the various types of membrane fouling as well as the effects of membrane cleaning. The objective of this comprehensive literature review is to reflect the current state of knowledge in the field of the removal of TrOCs by NF/RO focussing mainly on the last 3 to 5 years. Where necessary, relevant older references are included.

The main focus of the Chapters 2 and 3 is to delineate the effects of organic fouling of nanofiltration membranes on the rejection of the trace organic contaminant bisphenol A using synthetic wastewater. The particular impact of the calcium concentration in the feed solution and the respective mechanisms of solute transport under fouling conditions are discussed in detail.

Chapter 4 deals with the combined organic fouling (humic acid) and $CaCO_3$ scaling and the resulting impact on flux and on the rejection of TrOCs by a nanofiltration membrane. The results are compared to those observed under the conditions of pure $CaCO_3$ scaling. Again, the underlining mechanisms of solute rejection are elaborated.

In chapter 5 the findings of the studies conducted are briefly summarised, conclusions are drawn and a short outlook is given.

1.1 Fundamentals of NF/RO

The performance of NF membranes ranges between ultrafiltration (UF) and RO membranes. NF membranes are porous with sizes of the pores covering a range of 0.001-0.01 µm. Larger organic molecules, viruses, and particularly divalent salts are retained by NF membranes, so they are often used in water softening applications (Hilal et al. 2004, Lee et al. 2016, Oatley et al. 2012).

Unlike microfiltration (MF), UF, and NF membranes, RO membranes are so dense that they are considered as nonporous (Lee et al. 2016). The given pore size of approx. 0.0001-0.001 µm lies within the range of thermal motion of the polymer chains the membrane is made of. As a consequence, RO membranes are capable of rejecting low-molecular-weight species such as monovalent salts and organic molecules from aqueous solutions. The widely recognised mechanism of transport by RO is via diffusion through statistically distributed free volume areas. Initially, solvent and solutes dissolve into the membrane polymer (partitioning) followed by diffusion due to a concentration gradient driven by the applied pressure that exceeds the osmotic pressure. Separation occurs because of the difference in solubilities and mobilities of different solutes within the membrane. RO membranes are most frequently applied for the desalination of brackish groundwater or seawater and the production of potable water e.g. from treated wastewater. (Lee et al. 2016)

1.1.1.1 Solute transport through NF/RO membranes

There are basically two main transport mechanisms for the NF, namely convection and diffusion (Lee et al. 2016). The water flux for porous NF membranes is related primarily to the applied pressure (Δp), which can be described by the Hagen Poiseuille equation. In the case of high salt containing solutions, the osmotic pressure needs to be taken into account (Bandini and Vezzani 2003).

For convection, the water flux is dependent on the applied pressure, i.e. high pressure leads to high water flux as well as convective flux of solutes in the water (Lee et al. 2016). This is in accordance with the well-known transport mechanisms proposed by Spiegler & Kedem (1966). In contrast to convection, the diffusive transport (solute flux) is independent of pressure. Instead, diffusion is rather related to a solute concentration gradient across the membrane (Lee et al. 2016, Spiegler and Kedem 1966).

Solute transport through NF/RO membranes is often described using models based on the extended Nernst-Planck equation with the Donnan steric equilibrium at the membrane and solution interfaces (Bowen et al. 1997, Tsuru et al. 1991). The extended Nernst-Planck equation consists of three different components the solute flux is related to, namely the concentration gradient, the flux due to electrostatic forces (charge gradient), and the convection of the solute (volume flux). The importance of the solute concentration

c_i at the surface of the membrane in determining the solute passage becomes clear when considering the fact that all three terms contain c_i.

1.1.2 Separation mechanisms

1.1.2.1 Steric size exclusion

Membranes are capable of selectively separate solutes over a wide range of particle sizes and molecular weights/sizes, from macromolecular organic compounds to monovalent ions. Steric size exclusion or hindrance was shown to be the major rejection mechanism e.g. for hydrophilic compounds by NF (Dang et al. 2014a, Verliefde et al. 2008, Zazouli et al. 2009) and for disinfection by-products (DBPs) by RO (Doederer et al. 2014). In case of the neutral carbamazepine (CBZ) size exclusion even represents the exclusive rejection mechanism (Simon et al. 2013b). The great importance of the steric effect and the correlation of rejection by the HL membrane with molecular weight (MW) was reported for haloacetic acids (HAAs) and pharmaceutically active compounds (PhACs) (Kong et al. 2016). Simon et al. (2013a) show increasing steric hindrance and hence rejection of neutral hydrophilic TrOCs by NF with increasing equivalent width of the compounds. Size exclusion is also described as the dominating mechanism for the rejection of pharmaceuticals and personal care products (PPCPs) by NF/RO in the presence of silica fouling (Lin et al. 2014).

1.1.2.2 Donnan effect

The Donnan effect (or Gibbs-Donnan equilibrium) describes the uneven distribution of charged species between the two sides of a charged (semi-permeable) membrane, which is permeable to some, yet not all solutes in the solution (Donnan 1995). In this case, the permeable species distribute unevenly across the two sides of the membrane leading to a charge difference, the so-called Donnan potential, which consequently results in an additional osmotic pressure. As discussed, the interactions described before are only effective to charged solutes, i.e. salts or ionic organic compounds, whereas neutral solutes are naturally not affected by the Donnan effect.

1.1.2.3 Electrostatic repulsion

Another separation mechanism in membrane processes is electrostatic repulsion when addressing charged membrane surfaces and charged compounds under the given conditions of the feed water such as pH and ionic strength (IS) (Dang et al. 2014a, Lee et al. 2016, Verliefde et al. 2008, Zazouli et al. 2009). A membrane exhibits a charge due to the dissociation of ionisable groups in the active skin/surface layer of the membrane as well as within the membrane pores (Ernst et al. 2000, Hagmeyer and Gimbel 1998, Hall et al. 1997a, Hall et al. 1997b). These functional groups may be of acidic or basic type or even a combination of both depending on the materials utilised during the manufacture of the membrane. Taheran et al. (2016) concludes from literature that most of the available thin layer composite NF/RO membranes are negatively charged in neutral solutions due to deprotonation of the functional groups. Hence, the charge of TrOCs and the resulting electrostatic interaction with the membrane may contribute substantially to their rejection. For example, the rejection of sulfamethoxazole (SMX) (Simon et al. 2013b). However, for positively charged solutes a negatively charged membrane exhibits attractive forces, which leads to high concentrations at the membrane surface and consequently results in a lower observed rejection (Verliefde et al. 2007b). Electrostatic interaction may even affect uncharged compounds exerting a high dipole moment by aligning the molecule in a favourable direction toward the membrane pores and thereby promote the passage of the solute across the membrane (Nghiem et al. 2005a, Van der Bruggen et al. 1999, Van der Bruggen and Vandecasteele 2003).

1.1.2.4 Adsorption

In addition to the aforementioned separation mechanisms, TrOCs may also be rejected when they adsorb to the membrane polymer (Rana et al. 2014) or to adsorptive constituents (e.g. natural organic matter, NOM) in the feed water. A suitable fouling layer on the membrane surface could as well act as an adsorbent for TrOCs (Yangali-Quintanilla et al. 2009). Although the effect has been known for quite some time (Verliefde et al. 2008, Yangali-Quintanilla et al. 2009), various recent studies have discussed the importance of adsorption for the rejection of TrOCs by NF/RO membranes (Chen et al. 2014, Dang et al. 2014a, Kiso et al. 2014, Lin and Lee 2014, Liu et al. 2015, Wei et al. 2016).

Adsorption of TrOCs may be governed by chemical (hydrogen bonding, ionic or covalent) interactions and/or physical (hydrophobic) interactions (Muhamad et al. 2016b). These

authors also name adsorption the main rejection mechanism of TrOCs for MF and UF (Muhamad et al. 2016a). This was due to the fact that adsorption occurs not only on the membrane surface but also in the pores (Comerton et al. 2007). Adsorption often leads to a high initial rejection rate of TrOCs until an equilibrium stage is reached during which desorption occurs as well (Su-Hua et al. 2010).

1.1.3 Environmental applications of NF/RO

NF has been in the centre of interest of research and large scale applications for the treatment of groundwater, surface water, and wastewater reclamation/reuse for many years (Mohammad et al. 2015). Among traditional purposes like retaining divalent ions (water softening), removal of TrOCs such as pharmaceutically active compounds (PhACs), hormonally active agents, pesticides, etc. has increasingly become a new field of application for NF membranes. Due to very good removal capacities, lower energy consumption, less concentrate production and decreasing prices NF membranes have become an interesting alternative compared to RO. (Mohammad et al. 2015) However, RO (and low pressure reverse osmosis, LPRO) still remains an important membrane process to be applied when NF reaches its limitations, e.g. a sufficient removal of (small) organic compounds as shown in various studies (Azaïs et al. 2016, Fujioka et al. 2014a, Mahlangu et al. 2014a, Ogutverici et al. 2016) or meeting, for example, total organic carbon (TOC) requirements (Bellona et al. 2012).

1.1.4 Drinking water treatment from groundwater and surface water sources

Due to their separation capacities (e.g. dissolved organic carbon (DOC), colour, turbidity, UVA_{254}) and capability of producing large amounts of high-quality water NF/RO have been applied in the production of drinking water for many years (Garcia-Vaquero et al. 2014). For the treatment of groundwater the water softening capabilities, particularly of NF, as well as the removal of inorganic pollutants, e.g. arsenic, fluoride, radium, uranium are very favourable. Furthermore, as recent studies suggest, NF has increasingly been used in new applications e.g. the removal of persistent organic pollutants (POPs), pharmaceutical active compounds (PhACs) and hormones (Lopes et al. 2013, Madsen and Søgaard 2014, Pereira et al. 2012, Radjenovic et al. 2008, Saitúa et al. 2012, Sanches et al. 2012, Vergili 2013).

Madsen and Søgaard (2014) have studied NF/LPRO membranes for the treatment of pesticides polluted groundwater. The authors observed a rejection of >90% for regular pesticides by the NF99HF membrane tested. However, this NF membrane showed unsatisfactory rejection of pesticide transformation products (PTPs) due to a smaller molecular size of the solutes so LPRO was needed to provide a sufficient barrier for PTPs. Another study with a flat sheet NF membrane (FM NP010, Microdyn Nadir, Wiesbaden, Germany) in crossflow mode for PhACs removal for drinking water production from surface water found only moderate rejection rates, i.e. neutral carbamazepine was rejected by 31-39%, whereas ionic diclofenac (DIC) and ibuprofen (IBU) showed a better rejection rate with 55-61% (Vergili 2013).

The treatment of synthetic and river water contaminated with commercial formulations of the herbicide glyphosate by an NF pilot plant exhibited a rejection of >80% for the pesticide and the permeate to be free of acute toxicity towards fish (Saitúa et al. 2012). Comparing the molecular weight of the solute (168 Da) with molecular weight cut-off (MWCO) of the membrane (180 Da), the authors concluded that steric exclusion would have been less relevant a rejection mechanism. Thus, the fairly high rejection rate for glyphosate was attributed mainly to Donnan exclusion and dielectric exclusion due to the solutes high charge density. As a final conclusion, the authors classified NF a viable means for potable water treatment using glyphosate polluted surface water sources.

Ogutverici et al. (2016) studied the removal of triclosan (TCS) from a surface water used as a real drinking water source. The tested NF membrane DK-NF (GE Osmonics) rejected the biocide compound by only 57% due to its highly hydrophobic nature. In the presence of natural organic matter, an increased triclosan rejection was observed which was attributed to a TCS-HA complex formation. The authors also describe a positive correlation between the concentration of humic acid and the triclosan rejection.

A hybrid solar/wind-powered nanofiltration pilot plant was used to further treat a conventionally treated drinking water originating from a reservoir (surface) water (Garcia-Vaquero et al. 2014). The NF90 membrane exhibited a removal efficiency of >74% for most of the PhACs in the feed water. Several compounds like naproxen (NPX), diclofenac, ibuprofen and dilantin were rejected by the NF90 at rates ≥99%. That is a clear advantage over the conventional treatment which was not able to retain some PhACs such as carbamazepine and 1-hydroxyl-ibuprofen (metabolite of ibuprofen).

1.1.5 Water/Wastewater reclamation

The application of NF/RO membranes is becoming increasingly widespread in water treatment, industrial processes and wastewater reclamation/reuse due to the capacity of those membranes to provide a high product water quality (Bellona et al. 2012). Also, surface water augmentation and groundwater injection are interesting new fields in which NF/RO membrane processes may be applied.

Luo et al. (2014) have reviewed various treatment processes for TrOCs removal including NF and RO. They found removal efficiencies of NF membrane to be medium to high for PhACs, steroid hormones (SHs) and industrial chemicals (ICs) and medium for personal care products (PCPs). RO expectedly performed better with removal efficiencies to be medium to high for PhACs and high for PCPs, SHs, and ICs. Major process specific impact factors on efficiency were membrane properties such as pH, TMP and feed quality. The most important solute-related factors were hydrophobicity and molecular size. There are several disadvantages of NF/RO membrane processes, namely high energy demand, membrane fouling, and the disposal of concentrate (NF/RO) as well as desorption of sorbed chemicals from the membrane (NF) and the corrosive nature of the finished water (RO) (Luo et al. 2014).

1.2 Classification and materials of NF/RO membranes

1.2.1 Membrane classes

There are two classes of membranes: isotropic and anisotropic membranes. Isotropic membranes are characterised by a chemically and structurally homogeneous composition. Microporous membranes, nonporous dense films, and electrically charged membranes are typical examples of isotropic membrane (Baker 2004).

In contrast, anisotropic membranes are homogeneous in chemical composition (Loeb-Sourirajan membranes) with varying pore sizes and porosity across the membrane thickness or chemically and structurally heterogeneous (composite membranes) as described by Lee et al. (2016). The latter one exist as thin-film, coated films, and self-assembled structures. Composite membranes basically consist of a thin surface layer supported by a much thicker porous structure, the (mechanical) support layer. In some cases, a non-

woven backing layer provides additional mechanical support. These two or three structural parts of thin-film composite (TFC) membranes are mostly made of different polymeric materials. For example, the NF270 by Dow Filmtec (Minneapolis, MN, USA) consists of a polyamide active (PA) skin or surface layer (as thin as 20 nm) based on a polysulfone supporting (approx. 10 times the thickness of the skin layer) and a polyester backing layer (approx. a few µm thick) (Nghiem et al. 2005b, Semião and Schäfer 2013). The thin film or active skin layer exclusively determines the separation of solutes and permeation rates, whereas the porous supporting layer(s) solely provide mechanical support to the skin layer (Fujioka et al. 2015b, Lee et al. 2016). This structural design of TFC membranes leads to a high permeability/flux. According to Fujioka et al. (2015) TFC membranes are widely applied in NF/RO and have become the industry standard.

1.2.2 Membrane materials

Membranes can basically be made of three types of material: organic, inorganic or an inorganic-organic hybrid material. Looking at the published studies on TrOCs removal by NF/RO in water/wastewater treatment applications conducted between 2014 and 2016 the clear dominance of polymeric membranes, particularly polyamide membranes, is obvious as can be seen from Figure 1-1. There were no recent studies on hybrid membranes in the context of TrOCs removal so these type will not be described in detail.

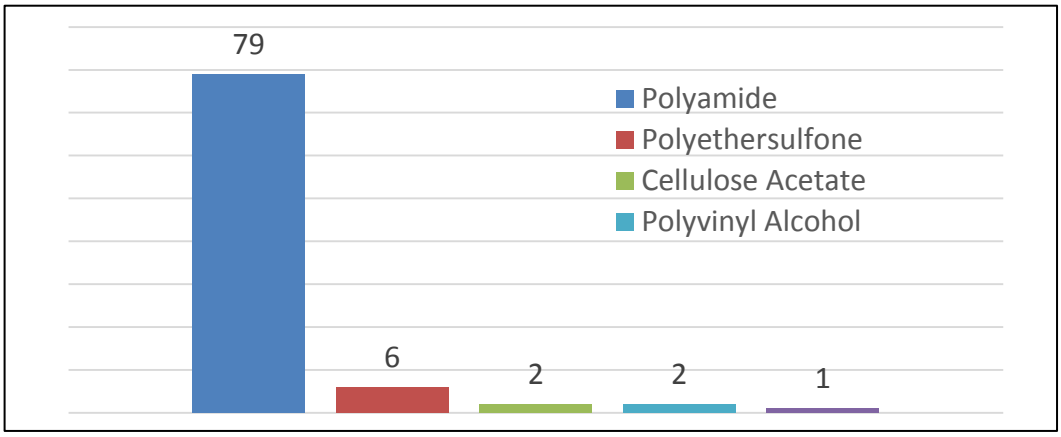


Figure 1-1: Numbers of membranes studied as a function of membrane material (active skin layer) between 2014 and 2016 (total number of membranes tested = 90)

1.2.3 Organic membrane materials

Essentially all organic membranes are made of polymeric materials. This is due to the fact that polymers offer a wide range of structure and properties. Typical polymeric materials for industrially established filtration membranes include cellulose acetates (CA), cellulose nitrate (CN), polyacrylonitrile (PAN), polyamide, polycarbonates (PC), polyetherimides (PEIs), polyimide (PI), polysulfone (PSU), polyethersulfones (PESs), cross-linked polyether, polypropylene (PP), polyvinylidene fluoride (PVDF), and polyvinyl alcohol (PVA). These membrane materials represent the first generation of polymeric materials and to date are most widely used in membrane applications (Lee et al. 2016, Ulbricht 2006).

1.2.3.1 Polyamide membranes

Supporting the abovementioned dominance of polyamide membranes it is reported that polyamide or polyamide-derivative RO membranes are used in most if not all water reclamation plants (Fujioka et al. 2012, Shenvi et al. 2015). This can be partly attributed to several favourable properties of polyamide membranes such as high permeate flux, adequate salt rejection and the opportunity to operate in a wide pH range (Lee et al. 2011). On the downside, polyamide membranes lack a sufficient resilience to strong oxidizing agents like free chlorine, which is used to control biofouling: This may lead to a chlorine-induced membrane degradation (Glater et al. 1994, Simon et al. 2009). However, the "membrane-friendly" surrogate anti-biofouling agent, monochloramine, is a precursor for the formation of disinfection by-products (e.g. N-Nitrosodimethylamine, NDMA).

1.2.3.2 Cellulose acetate membranes

Cellulose acetate and cellulose triacetate (CTA) have re-emerged as membrane material for RO especially for feed waters with high fouling potential. This is due to the chlorine resistance (up to 1 ppm) so therefore chlorine can be used to suppress the biofouling on the membrane surface (Shenvi et al. 2015). Cellulose acetate-based membranes exhibit a significantly lower surface charge than polyamide based RO membranes. Consequently, the role of electrostatic repulsion of charged TrOCs is less significant compared to polyamide RO membranes (Fujioka et al. 2015a). However, the knowledge regarding the rejection of TrOCs by cellulose acetate membranes in RO applications remains very scarce

due to the lack of respective studies. The abovementioned chlorine resistance of CA/CTA membranes is still accompanied by a disadvantage, namely a limited permeate flux (Konagaya et al. 2001). Another disadvantage of CA/CTA membranes is the very narrow tolerable operational pH range (4 to 6) (Shenvi et al. 2015), because outside this range CA membranes are prone to hydrolysis both in acidic and alkaline conditions (Vos et al. 1966).

1.2.4 Inorganic membrane materials

On the other hand, inorganic membranes have recently attracted a lot of interest due to their favourable material properties such as thermal, chemical, and mechanical robustness as well as their reusability. Membrane treatment of wastewater is often subject to high fouling potential and consequently requires chemical cleaning. That offers new opportunities for the application of, for example, ceramic membranes that show greater fouling-resistance (Lee et al. 2016), since they are described as hydrophilic membranes with lower hydrogen bonding potential than polymeric membranes (Childress and Elimelech 1996). The greater chemical stability/resilience and the longer life of ceramic membranes compared to current polymeric membranes make them an interesting option for e.g. drinking water applications and provide reliability and safety (Fujioka et al. 2014a, Lee et al. 2016). Loose ceramic membranes (MWCO > 500 Da) have been commercially available for more than a decade. Very recent developments in ceramic materials and manufacturing technologies facilitated the production of much tighter ceramic membranes, e.g. MWCO = 200 Da (Fujioka et al. 2014a). Furthermore, TiO_2 as an important material for the manufacture of ceramics is considered a nontoxic, readily available, and inexpensive material (Lee et al. 2016). On the other hand, Fujioka et al. (2014) state the low permeability, relatively high capital cost and the limited availability of low MWCO membranes as limiting factors for a wider use of ceramic membranes.

Membrane materials currently developed usually feature nanocrystalline structures, including porous ceramics (e.g. Al_2O_3, TiO_2, ZrO_2, ZnO, and SiO_2,), composites containing two or more materials (e.g. TiO_2–SiO_2, TiO_2–ZrO_2, and Al_2O_3–SiC), and various nanoparticle composites (e.g. Ag–TiO_2, Zn–CeO_2, and zeolites (DeFriend et al. 2003, Kumar et al. 2014, Lee et al. 2016, Mohmood et al. 2013).

1.3 Removal of trace organic contaminants

The rejection capacity of NF/RO membranes for organic solutes like TrOCs is a highly complex matter which is impressively demonstrated in Figure 1-2. There are numerous factors affecting rejection efficiency of TrOCs by NF/RO, which can be classified into four groups: 1. Membrane characteristics, 2. Feed solution characteristics, 3. Solute characteristics, and 4. Operational characteristics. Additionally, membrane fouling as well as membrane cleaning play an important role in determining the rejection of TrOCs from an aqueous solution using NF/RO membranes. Taking the aforementioned complexity of the topic into account, rejection mechanisms and their interrelation will be discussed in detail in the following sections.

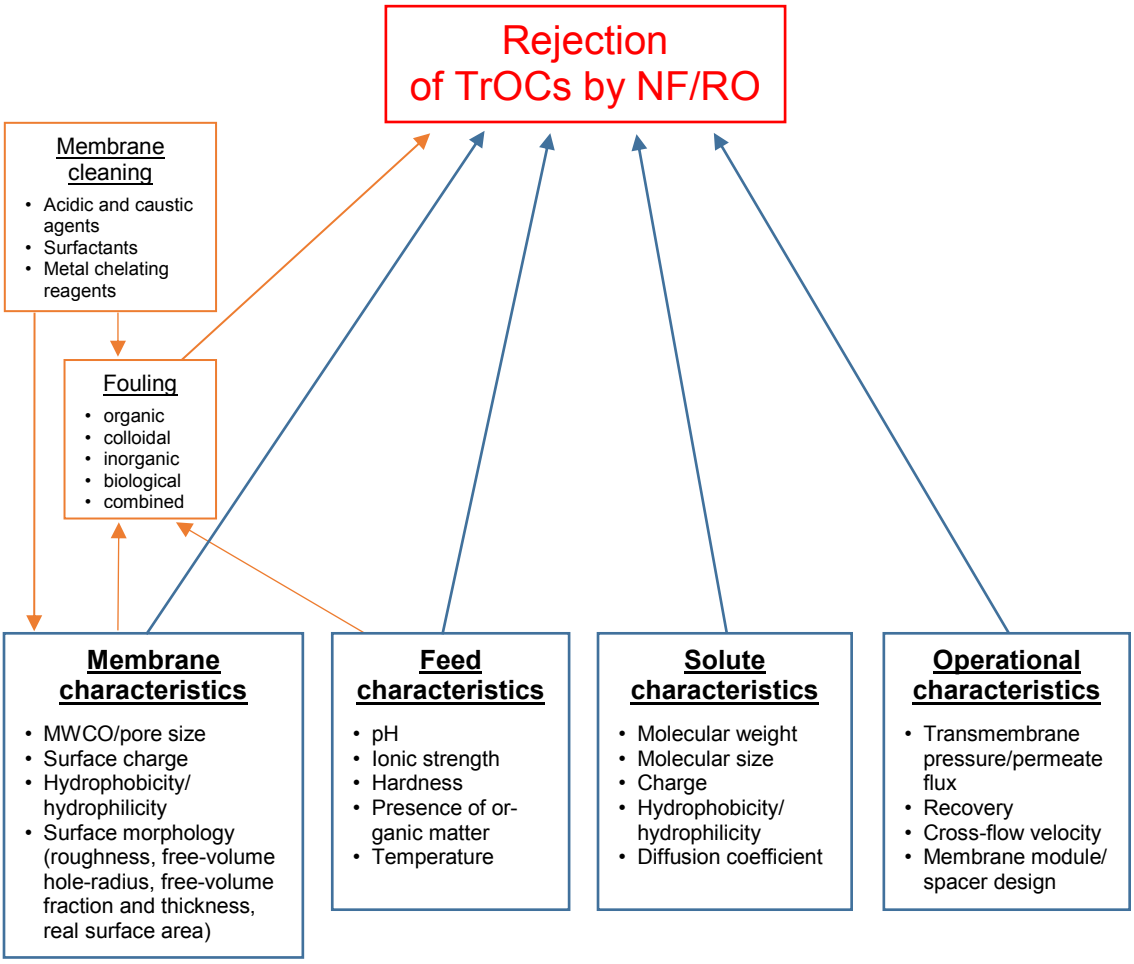


Figure 1-2: Schematic diagram showing the complexity of various impact factors on the rejection of trace organic compounds

Table 1-1 gives an overview of rejection rates of various types of TrOCs observed for NF/RO membranes and aims at underlining the large variation TrOC rejection is subject to. The range of variation may be due to the abundance of parameters affecting NF/RO membrane filtration (as shown in Figure 1-2). This is also reflected by the various experimental conditions studies are conducted under, which complicates the comparison of the results.

Table 1-1: Selection of rejection rates of various types of TrOCs for NF/RO membranes

Compound/ Group of compounds	Membrane					Scale tested	Range of rejection (%)	Comment/ Operational conditions	References
	Type	Material	loose NF	tight NF	RO				
Pharmaceutical active compounds									
Various	NF270	PA	X			Lab	**20 - 90**	WWTP effluent and electrolyte solution	Azais et al. (2016)
Various	NF90	PA		X		Lab	**> 80**	WWTP effluent and electrolyte solution	Azais et al. (2016)
Carbamazpine	NF270	PA	X			Lab	**60**	Clean membrane	Mahlangu et al. (2014a)
Carbamazpine	NF270	PA	X			Lab	**18**	Organically fouled membrane, no flux correction!	Mahlangu et al. (2014a)
Carbamazpine	NF270	PA	X			Lab	**24**	Colloidally fouled membrane, no flux correction!	Mahlangu et al. (2014a) Mahlangu et al. (2014a)
Caffeine	NF270	PA	X			Lab		Clean membrane	Mahlangu et al. (2014b)
Various	NF270	PA	X			Lab	**35 - 90**	Clean membrane	Mahlangu et al. (2016)
Various	NF90	PA		X		Pilot	**28 - 100**	Conventionally treated drinking water; system recovery = 70%	Garcia-Vaquero et al. (2014)
Personal care products									
Triclosan	DK-NF	PA	X			Lab	**57**	Surface water	Ogutverici, et al. (2016)
Disinfection by-products									
Various	ESPA2	PA			X	Lab	**0 - 98**	Feed temperature 33,5 °C	Doederer, et al. (2014)
Various	ESPA2	PA			X	Lab	**21 - 99**	Transmembrane flux 3 L/m²·h	
Various	ESPA2	Pa			X	Lab	**25**	Feed temperature 35 °C	
N-Nitrosamines (neutral)	HKC3023V	CTA			X	Lab	**25 - 78**	Feed: electrolyte solution	Fujioka, et al. (2015a)
N-Nitrosamines (neutral)	TFC 4040HR	PA			X	Pilot	**27 - 95**	RO system recovery = 25%	Fujioka, et al. (2014c)
N-Nitrosamines (neutral)	TFC 4040HR	PA			X	Pilot	**10 - 89**	Feed temperature = 35 °C	Fujioka, et al. (2014c)
THM	NF90, spiral wound	PA		X		Pilot	**53**	Conventionally treated drinking water; system recovery = 70%	Garcia-Vaquero et al. (2014)
Trace organic contaminants, miscellaneous									
Various (neutral hydrophilic)	HKC3023V	CTA			X	Lab	**25 - 78**	MW 74 - 130 g/mol	Fujioka, et al. (2015a)
Various (neutral hydrophobic)	HKC3023V	CTA			X	Lab	**> 95**	MW > 236 g/mol	Fujioka, et al. (2015a)
Diuron (neutral, hydrophobic)	HKC3023V	CTA			X	Lab	**39**	MW = 233	Fujioka, et al. (2015a)
Various (neutral hydrophilic/hydrophobic)	IKTS	Ceramic	X			Lab	**20 - 92**	Feed: electrolyte solution	Fujioka, et al. (2014a)
Various (neutral hydrophilic/hydrophobic)	NF270	PA	X			Lab	**5 - 98**	Feed: electrolyte solution	Fujioka, et al. (2014a)
Various (neutral hydrophilic/hydrophobic)	NF90	PA		X		Lab	**6 - 99**	Feed: electrolyte solution	Fujioka, et al. (2014a)
Various (charged)	HKC3023V	CTA			X	Lab	**> 90**	Feed: electrolyte solution	Fujioka, et al. (2015a)
Various (charged)	IKTS	Ceramic	X				**25 - 99**	Feed: electrolyte solution	Fujioka, et al. (2014a)
Various (charged)	NF270	PA	X				**58 - 99**	Feed: electrolyte solution	Fujioka, et al. (2014a)
Various (charged)	NF90	PA		X			**89 - 100**	Feed: electrolyte solution	Fujioka, et al. (2014a)
Volatile organic carbons	BW30				X	Pilot	**3 - 99**	Secondary effluent, UF pretreated	Martinez et al. (2015)
Odors	BW30	PA			X	Pilot	**5 - 99**	Secondary effluent, UF pretreated	Martinez et al. (2015)
Allergens	BW30	PA			X	Pilot	**90 - 98**	Secondary effluent, UF pretreated	Martinez et al. (2015)
Perfluorinated organic compounds									
Various	loose	various			X	Lab	**88 - 98**	pH = 7	Chen, et al. (2014)
Various	tight	various			X	Lab	**98,5 - 100**	pH = 3 - 9	Chen, et al. (2014)
Polycyclic aromatic hydrocarbons									
Naphthalene	DK	PA		X		Lab/pilot	**29**	Industrial w/w; TMP = 20 bar, Temperature feed = 25°C	Efligenir et al.(2014)
Pyrene	DK	PA		X		Lab/pilot	**40**		Efligenir et al.(2014)
Phenanthrene, Fluoranthene, Chrysene	DK	PA		X		Lab/pilot	**100**		Efligenir et al.(2014)
Endocrine disrupting compounds									
Tributylphosphate	BW30	PA			X	Pilot	**99**	Secondary effluent, UF pretreated	Martinez et al. (2015)
Alkylphenols (NP2EO, OP1EO, OP2EO)	DK	PA		X		Lab/pilot	**>84 - 97**	Industrial w/w; TMP = 20 bar, Temperature feed = 25°C	Efligenir et al.(2014)

1.3.1 Impact of membrane characteristics

1.3.1.1 Molecular weight cut-off/pore size

The MWCO value of a membrane refers to the molecular weight of a molecule or solute of which 90% is rejected by the membrane. The actual pore size of a membrane (in nm or µm) can be determined from the MWCO. According to Lee et al. (2016) pore sizes of NF and RO membranes (although RO membranes are considered nonporous) range from 0.001 - 0.01 µm and 0.0001 - 0.001 µm, respectively. This relates to approximate MWCO values ranging from 200 to 1,000 Da for NF and <200 for RO membranes (Yoon 2017).

The MWCO is not a standardised measure and it is always solute specific. Additionally, the concept is based on the consideration of the solute being round in shape. However, particularly large organic molecules often have a lengthy shape and might be able to penetrate a pore when they approach it with their small size first. In such cases, the MW of the solute might have suggested a high(er) rejection as is effectively observed.

As discussed in section 1.1.2.1, size exclusion is one of the most important mechanisms governing the rejection of solutes by a membrane. Pore size is directly correlated to rejection of a solute so changes to the pore size can clearly affect rejection. As Dang et al. (2014b) and Doederer et al. (2014) report, pore size is subject to change with feed temperature. Also, pH, ionic strength, and the presence of divalent ions can influence the pore size which is discussed in detail in section 1.3.2.

Another interesting fact is the impact of the pore size on adsorption of mainly hydrophobic solutes (Dang et al. 2014a). Small pores prevent the solute to enter/penetrate into the pores so adsorption occurs on the membrane surface only. This limits the diffusion of the solute across the membrane which leads to a higher rejection.

1.3.1.2 Surface charge

The surface charge of a membrane is determined by the chemical structure, i.e. the type and abundance of functional groups in the active skin layer. The type of surface charge (positive or negative) and charge intensity of a membrane are determined by the chemical structure and the existence and type of functional groups (Bellona et al. 2004). The surface

charge exerts a great influence on rejection of charged solutes (due to the charge repulsion effect) and is subject to change with feed pH (Chen et al. 2014, Doederer et al. 2014, Fujioka et al. 2014c). A more detailed discussion can be found in section 1.3.2.1

1.3.1.3 Hydrophobicity/hydrophilicity

Hydrophobicity and hydrophilicity of a membrane are used to describe their attraction or absence thereof for solutes in the feed solution to adsorb to the membrane surface (Muhamad et al. 2016b). The hydrophobicity/hydrophilicity of a membrane is mainly determined by the type and abundance of the functional groups in the membrane polymeric matrix, strongly depend on pH and are closely associated with the hydrophobicity/hydrophilicity of the solutes. Hydrophobic interactions may occur between a solute and the membrane surface or even the surface of a covering fouling layer (Azais et al. 2014, Bellona et al. 2010, Comerton et al. 2009, Mahlangu et al. 2014a). The impact of the hydrophobicity/hydrophilicity of a membrane on the rejection behaviour of TrOCs by NF/RO will be discussed in detail in section 1.3.1.3.

The influence of fouling on hydrophobicity/hydrophilicity has been shown in several studies. Lin et al. (2014) reported a more hydrophilic membrane surface due to a colloidal fouling layer. In contrast, Simon et al. (2013b) did not observe an impact on hydrophobicity by silica colloidal fouling (Simon et al. 2013b). These authors observed, however, a significant hydrophobisation of the membrane surface by organic fouling. An increase of the membrane hydrophobicity also occurred after chemical cleaning (Simon et al. 2012, 2013c). This was attributed to conformational modifications of polymeric matrix due to harsh cleaning regime, adsorption of metal chelating agents of the cleaner rendering the surface more hydrophobic, and residues of organic foulants.

1.3.1.4 Surface morphology

Roughness and (real) surface area

The roughness of a membrane surface in general is dependent on the size, shape, frequency, and distribution of the surface projections (Hobbs et al. 2006). Roughness correlates with the surface area of the membrane i.e. a rough surface leads to a larger surface

area than a smoother membrane. Hence, a rougher surface morphology results in increased adsorption of TrOCs due to more opportunities for molecular contact (Comerton et al. 2007, Dang et al. 2014a, Li et al. 2007).

The potential impact of the surface area of the active skin layer of an RO membrane on rejection of neutral solutes was shown by Fujioka et al. (2015b). According to the authors, the apparent surface area for both a low and a high roughness membrane is equal. However, the rough membrane exhibits a larger real surface area due to a local (micrometre scale) roughness, whereas for a smooth membrane apparent and real surface area are similar. Hence, their real local water flux is similar to the experimental water flux. For the rough membrane the larger real surface area leads to a higher permeability and thus a lower local water flux may occur although the apparent experimental water flux is identical to that of the smooth membrane. Consequently, the decreased local water flux leads to a decrease in solute rejection, which is in accordance with the irreversible thermodynamics model. (Fujioka et al. 2015b)

Furthermore, colloidal fouling can be correlated with the surface roughness of nanofiltration and reverse osmosis membranes (Hoek et al. 2003, Vrijenhoek et al. 2001). The studies showed that in the initial stages of fouling, the colloidal particles preferentially accumulated in the “valleys” of rough membranes, leading to “valley clogging”. Therefore, a rough membrane generally is more prone to fouling than a smooth membrane. The implications of colloidal fouling on TrOCs removal by NF/RO are discussed in section 1.3.5.2.

Free-volume hole-radius/size

As Fujioka et al. (2015b) conclude from literature, the presence of free-volume holes between cross-linked polymer chains of the active skin layer of a membrane is widely accepted. Water molecules and small solutes may partition into these free-volume holes. Particularly for neutral and hydrophilic solutes (e.g. NDMA) the free-volume hole-size is expected to be the most important factor governing rejection by RO.

In addition to the free-volume hole size other membrane characteristics such as the free-volume hole-size distribution (Fujioka et al. 2013c), the free-volume fraction and active skin layer thickness (Fujioka et al. 2015b) may also play an important role in the rejection of small and uncharged solutes by RO membranes.

Free-volume fraction and active skin layer thickness

Fujioka et al. (2015b) reported that an increase in free-volume fraction of the active skin layer of RO membranes results in an increase of the diffusivity of water and solutes, which consequently improved water permeability and solute permeation as well. The basic solution-diffusion model indicates a dependence of solute rejection on thickness (Bandini and Bruni 2010). Additionally, it was shown with an extended solution-diffusion model featuring the concept of free volume-holes that thickness and free-volume fraction as well as free-volume hole-radius determine solute rejection (Wang et al. 2014).

1.3.2 Impact of feed characteristics

1.3.2.1 pH value

According to Dang et al. (2014a) the feed solution pH is one of the most important parameters influencing the hydrophobicity, the adsorption, and the chemical speciation of dissociable organic compounds as well as the membrane surface charge. Possible changes to the membrane structure occurring with changing pH are reported in the literature (López-Muñoz et al. 2009). This structural change is caused by stronger electrostatic interactions between the dissociated functional groups resulting in pore shrinkage at high pH. In contrast, other studies showed an increase in pore size with increasing pH (Donose et al. 2013, Simon et al. 2013a).

Doederer et al. (2014) described a decrease of permeability with increasing pH for the NF membrane but not for the RO membrane tested, respectively. For NF membranes the rejection on inorganic solutes (salts) is governed by size exclusion and Donnan exclusion. With increasing pH the membrane surface charge turns more negative as well which leads to Donnan exclusion becoming the dominant mechanism of rejection. In contrast, for RO membranes size exclusion is the dominant mechanism of rejection so an increase in membrane surface charge with increasing pH plays no or only a minor role. For organic compounds, namely polar DBPs a slight increase of rejection at increased pH was observed. The authors assume that transport through the membrane is facilitated by H-bonding between membrane polymer and DBPs. Increased hydroxide concentrations at high pH may interfere with H-bonding between membrane and solute resulting in a rise of rejection. In contrast, no effect of pH changes was seen for hydrophobic DBPs. Since adsorption is considered the main rejection mechanism, minor changes of surface charge

and pore size due to changing pH is not affecting adsorption. Similar to the aforementioned study Fujioka et al. (2014b) observed a small increase of rejection for NDMA (9%) with a large pH shift from 5 to 9.5; but only negligible effect for other N-nitrosamines. In contrast, a clear effect of solution pH on rejection of perfluorinated organic compounds (PFCs) ($pK_a \approx 3$) was shown particularly for loose/low desalting LPRO membranes. In fact, rejection was low at pH 3 due to the ineffectiveness of electrostatic repulsion. Under this condition, PFCs are only slightly charged and the membrane's charge ranges around the point of zero charge (isoelectric point). Hence, at low pH mainly size exclusion affects rejection. With increasing pH PFCs dissociate and membrane charge gets increasingly negative, which consequently leads to increasing charge repulsion and thus increasing rejection (Chen et al. 2014). An indirect effect of pH in the presence of organic matter (hydrophobic acid organic matter, HpoA) was described by Jin & Hu (2015), who observed an increase in the rejection of estrone when the pH was raised from 7 to 10.4. Even though 50% of estrone was dissociated the charge effect was not so pronounced. Instead, the HpoA played an important role since it showed an extended conformation at high pH. This resulted in a strong association of the undissociated 50% fraction of the estrone with HpoA. Since HpoA was well rejected by size exclusion a high rejection for estrone was observed as well.

1.3.2.2 Ionic strength

The impact of the ionic strength of a feed solution on NF/RO membrane filtration, namely the screening of the membrane charge, was already reported more than a decade ago (Schäfer et al. 2003). Another effect was described in the literature, showing the reduction of the hydrodynamic radius of polar solutes under high ionic strength conditions, which led to a smaller apparent solute size (Bargeman et al. 2005).

More recent studies found no discernable impact of IS on DBPs rejection by either NF or RO except a small increase by 15% in the rejection of dichloroacetamide by NF when IS was raised from 7 to 70 mM (Doederer et al. 2014). Haloacetamides (HAcAMs) may interact with the membrane polymer by H-bonding. Additionally, the membrane's negative charge may direct the opposite charge of the compounds dipole towards the surface and in that way facilitate entry into the pore and thereby promote transport across the membrane. In case of high ionic strength increased shielding of the negative charges of the membrane by counter ions in solution as well as the compression of the electric double

layer are resulting in a reduced surface charge. Thereby interaction of HAcAMs with the membrane is reduced leading to improved rejection. The shielded membrane charge may also result in less directing of the compound's dipole towards the membrane surface and into the pores, which consequently increases rejection. Regarding RO it was assumed that the impact was perhaps too small to show significant changes in DBP rejection by RO. (Doederer et al. 2014)

Another impact of solution ionic strength was reported by Jin & Hu (2015) who studied estrone rejection by NF in the presence of hydrophobic acid organic matter (HpoA). At neutral pH the ability of HpoA macromolecules to improve estrone rejection became stronger with increasing ionic strength due to their more extended conformation, which created more chances for the association between estrone and HpoA.

1.3.2.3 Organic matter

The impact of organic matter (e.g. effluent organic matter, EfOM) in the feed water on the rejection of TrOCs by NF/RO has been known for quite some time and studied extensively (Azais et al. 2014, Comerton et al. 2009, Feng et al. 2014, 2015, Jin et al. 2007, 2010, Jin and Hu 2015, Nghiem et al. 2008, Nghiem and Hawkes 2007, Nghiem et al. 2005a, Nghiem et al. 2005b, Zazouli et al. 2009). Jin & Hu (2015) identified hydrophobic acid organic matter as the organic fraction with the most crucial impact on the enhancement of estrone rejection by NF/RO. In their most recent study, it was shown that the rejection of estrone by NF significantly improved in the presence of hydrophobic acid organic matter (HpoA) at all pH and ionic strength levels. At neutral or alkaline pH this enhancement effect is governed by steric size exclusion due to binding of estrone to the HpoA macromolecules by hydrogen bonding as well as charge repulsion. Azais et al. (2014) observed an improvement of rejection for PhACs when filtering MBR effluent compared to Milli-Q water particularly for loose NF membranes. The increase in rejection was attributed to solute-solute interactions by hydrogen bonding and hydrophobic interactions between the organic compounds and organic macromolecules (EfOM), which consequently led to enhanced sieving effects. Similar observations were reported for the removal of triclosan from a real surface water with added humic acid due to TCS-HA complexation (Ogutverici et al. 2016). Although simultaneously occurring cake-enhanced concentration polarisation affected PhACs rejection, the CECP mechanism is offset by the above mentioned enhanced sieving

effects due to the formation of EfOM-PhAC complexes and hence the PhACs removal increases (Azais et al. 2014).

1.3.2.4 Presence of divalent ions

The presence of divalent ions and particularly Ca^{2+} (also referred to as “calcium”) and the resulting impact on TrOCs removal by NF/RO has also been studied extensively (Azais et al. 2014, Mahlangu et al. 2014a, Mahlangu et al. 2014b, Mo et al. 2015). In a recent study, Mahlangu et al. (2014) showed the impact of Ca^{2+} on organic and colloidal fouling. The addition of $CaCl_2$ altered the fouling layer (Azaïs et al. 2016, Mahlangu et al. 2016) and reduced CECP effects (Mahlangu et al. 2016). Furthermore, aggravated fouling occurred in the presence of calcium due to specific organic-calcium complexation (Mahlangu et al. 2016). The impact of the presence of divalent ions is discussed in more detail in section 1.3.5 (Fouling).

1.3.2.5 Presence of foulants

The feed water of a membrane process may contain constituents showing the potential of causing membrane fouling. These can be organic matter, colloids, salts (carbonates, sulfates), and constituents promoting biological fouling. The effects caused by these constituents in the feed water will be discussed in detail in section 1.3.5 (Fouling).

1.3.2.6 Temperature

The feed temperature for a membrane process in wastewater reclamation and drinking water treatment may be subject to considerable seasonal variation and also substantially depends on the geographical location of the treatment plant (hot or cold climate). The importance of this fact is emphasised by several reports on the impact of temperature on the rejection of TrOCs. (Dang et al. 2014b, Doederer et al. 2014, Fujioka et al. 2014c)

The feed temperature was shown to exert a significant impact on membrane pore radius of the NF270 membrane which increased from 0.39 to 0.44 nm when the temperature

rose from 20 to 40 °C (Dang et al. 2014b). This effect was attributed to a thermal expansion of the membrane polymer as well as an additional alteration of the thickness and porosity of the active layer.

Dang et al. (2014b) also note that with increasing temperature of the feed solution, an increase of permeability due to a decrease of water viscosity occurred. A great impact on rejection, namely a decrease was observed for neutral solutes due to less effective size exclusion. Also, there was an impact of temperature on rejection of negatively charged TrOCs, particularly smaller ones, but it was less pronounced than for neutral TrOCs. In addition to the reported rise in pore size, an increase of the diffusion coefficient with increasing temperature leading to lower rejection was observed. There seems to be also a greater impact of solution temperature on the rejection of moderately rejected solutes. (Dang et al. 2014b)

Similar to Dang et al. (2014b), Fujioka et al. (2014b) also discovered a considerable impact of solution temperature when testing the rejection of N-nitrosamines in a RO pilot scale study and thereby confirmed the results of a previous lab-scale study. When rising the feed temperature from 10 to 35 °C the rejection considerably dropped by up to 50%, particularly for small to medium sized N-nitrosamines. For cold climates (10 °C) the rejection of NDMA was 40%; other N-nitrosamines were rejected by more than 80%. In contrast, for hot climates (wastewater temperature 30 to 35 °C) rejection of NDMA was negligible, while the other N-nitrosamines exhibited a rejection of 30 to 80%. The observed changes of rejection with changing feed temperature confirm that the active skin layer or separation layer of the RO membrane is subject to change its physicochemical characteristics (Sharma et al. 2003). Furthermore, the drop of solute rejection can be attributed to increasing permeability coefficients of the solutes due to increasing feed temperature (Tsuru et al. 2010).

In accordance with the abovementioned studies Doederer et al. (2014) also reported a considerable drop of rejection with increasing temperature and discuss a number of mechanisms in order to explain their observations. An increase of pore size with increasing temperature due to polymer relaxation (Sharma et al. 2003) was assumed, which was supported by the observed increase of permeability after correcting for viscosity. This affects mainly neutral solutes due to a reduced size exclusion effect, which confirms the abovementioned observations of Dang et al. (2014b). The impact of temperature increase on rejection was greater for compounds of smaller molecular volume/width since these particularly benefit from easier entry into the membrane matrix due to an expanded pore

size. Additionally, an increased diffusion rate into the membrane matrix as a result of the lower viscosity of the feed solution may also contribute to a reduced DBP rejection. Increased partitioning at high temperatures (Tan et al. 2002) was assumed to explain the higher sensitivity of iodinated trihalomethanes (I-THMs) to temperature changes than other DBPs.

1.3.3 Impact of solute characteristics

1.3.3.1 Molecular weight

Depending on the MWCO of the membrane, the MW is an important first indicator whether a solute will be rejected or permeate through that membrane. Generally, rejection increases with increasing MW (Chen et al. 2014, Dang et al. 2014a, Fujioka et al. 2014c, Kong et al. 2016), however, exceptions exist. The MW is most important for neutral solutes, particularly hydrophilic ones (Fujioka et al. 2015a). Similar findings were reported by Simon et al. (2013a) who showed that rejection of neutral hydrophilic and moderately hydrophilic neutral TrOCs (log_D > 3) by the NF270 and NF90 membranes is predominantly governed by the membrane porosity and the MW of the TrOCs. Chen et al. (2014) observed a large influence of MW on rejection, particularly for loose and low desalting LPRO membranes. However, the authors state rejection may be better explained by consideration of molecular size (height/width, see section 1.3.3.2 below) in addition to molecular weight.

1.3.3.2 Molecular size (length and width)/molecular volume

As discussed in the previous section MW is an important parameter for the evaluation of the rejection potential of a membrane for a given solute. However, MW does not always correlate with the actual size, i.e. molecular length and width of a molecule. Therefore it is essential to know the molecular size parameters in addition to MW. This was reported by Chen et al. (2014), who observed a good correlation of MW with molecular length (ML) for PFCs and non PFCs. Hence, there was a large influence of molecular length/width on the rejection of PFCs and non PFCs, particularly for the loose low desalting LPRO membrane. An increase of rejection of hydrophilic neutral and hydrophilic negatively charged compounds with increasing molecular width was shown by Dang et al. (2014a). Another

study found that of the various physicochemical parameters studied, molecular volume shows the best correlation with permeate flux and rejection of pesticides and derivatives for the NF90 membrane tested (Hidalgo et al. 2016).

1.3.3.3 Minimum projection area/Equivalent width

The minimum projection area (MPA) is a relatively new parameter and it was first used to correlate compound size and rejection (e.g. Fujioka, et al. 2015a). These authors carried out a study with RO membranes of different membrane materials, namely polyamide, the most widely used material for NF/RO, and cellulose triacetate. They observed a good correlation of the rejection of n-nitrosamines with MPA for the polyamide RO membrane. For the cellulose triacetate RO membrane correlation of rejection of n-nitrosamines with MPA showed to be worse than for the polyamide RO membrane since the largest compounds, N-nitrosodipropylamine (NDPA) and N-nitrosodi-n-butylamine (NDBA), did not fit the correlation curve. The authors assumed these compounds might adsorb more progressively leading to an increased diffusion across the membrane and consequently a decreased rejection.

Simon et al. (2013a) correlated the rejection of hydrophilic and moderately hydrophilic neutral TrOCs by NF270 and NF90 membranes to their molecular dimensions, namely equivalent width, which is 'defined as √S/2, where S is the minimum area of a rectangle enclosing the projection of the molecule on the plane perpendicular to the length-axis'. The rejection of the studied TrOCs increased with their equivalent width due to steric hindrance.

1.3.3.4 Charge

Charge is a quantitative measure of the strength of an acid in solution i.e. the larger pK_a the smaller the extent of dissociation at any given pH. Therefore, the pK_a value of a compound is a particularly important parameter in relation to the feed pH. Solutes that dissociate in the range of feed pH become ionic. As a consequence, electrostatic interactions between solutes and a (charged) membrane surface come into effect. These electrostatic interactions, often referred to as charge repulsion, is an important rejection mechanism that is entirely ineffective to neutral compounds (Dang et al. 2014a).

Chen et al. (2014) showed a greatly enhanced rejection of PFCs in dissociated state, PFCs are ionic at pH > 3, by a significantly greater efficacy of electrostatic exclusion. The authors also observed a greater influence of the electrostatic charge effect for loose membranes (Chen et al., 2014). In pH experiments with the NF270 and ESPA2 membranes Dang et al. (2014a) observed higher rejections for most charged TrOCs compared to neutral species, which was attributed to electrostatic repulsion.

1.3.3.5 Hydrophobicity/hydrophilicity

Some basic information on hydrophobicity/hydrophilicity of membranes has already been given in section 1.3.1.3. These are generally applicable to solutes as well.

Hydrophobicity and hydrophilicity of a solute are used to describe their attraction or absence thereof to adsorb to a membrane surface. Hydrophobicity and hydrophilicity strongly depend on pH and are closely associated with hydrophobicity/hydrophilicity of the membrane surface or even the surface of a covering fouling layer.

Chen et al (2014) showed the impact of hydrophobic adsorption on the rejection of PFCs particularly for loose membranes for which the size exclusion effect is less pronounced. A high hydrophobic adsorption of the solutes to the membrane surface was proposed as an initial rejection mechanism. However, the authors suggested a possible slippage of PFCs through the membrane, partially due to the slender molecular structure of these compounds. Governed by steric forces and/or diffusion a lower overall rejection for hydrophobic compounds was observed. In contrast, hydrophilic NFCs were better retained since they did not adsorb to the membrane. A similar observation, i.e. an increase of rejection with increasing hydrophilicity was reported by Dang et al. (2014a). On the other hand, hydrophobic TrOCs adsorbed to the membrane surface which led to increased partitioning of these compounds into the membrane. Consequently, a rise in transport through the membrane occurred resulting in a lower rejection (Dang et al. 2014a). However, these authors did not see a strong correlation between adsorption and the hydrophobicity of TrOCs. Additionally, there was no correlation between adsorption and $\log_D$ (both for hydrophilic and hydrophobic compounds). This was attributed to the existence of other impact factors (physicochemical characteristics of TrOCs and the membrane material), such as molecular size and charge of the compounds as well as pore size, charge, and surface roughness properties of the membranes. These parameters exerted a considerable influence on the adsorption of TrOCs to the membranes. (Dang et al. 2014a)

1.3.4 Impact of operational characteristics

1.3.4.1 Transmembrane pressure/permeate or transmembrane flux

The transmembrane pressure (TMP) is the driving force that facilitates the separation process in membrane systems like NF/RO. TMP is the pressure difference between feed and permeate stream. The permeate flux or transmembrane flux (TMF) is according to Darcy's law directly proportional to the TMP.

Rejection of solutes is largely influenced by TMP/TMF, which generally results in an increase in rejection with increasing TMP/TMF (Doederer et al. 2014, Fujioka et al. 2013b, Fujioka et al. 2014c, Kong et al. 2016). This is in accordance with the irreversible thermodynamics model, which states that the increase in water flux is larger than that of the solutes (Fujioka et al. 2013b, Fujioka et al. 2014c). As stated above, rejection increased with increasing TMP for all DBPs, except for triiodomethane (TIM) for the RO membrane and TIM and bromodiiodomethane (BDIM) for the NF membrane (Doederer et al. 2014). For these adsorptive compounds, e.g. the iodo-THM, their increased solute–membrane affinities led to a lower range of rejection as a function of flux since their diffusive flux increases with the water flux. This effect was proposed by Déon et al. (2013) who showed an increase of solute concentration on the membrane surface with increasing pressure (that induces increasing flux) leading to a higher concentration gradient and consequently a decrease in rejection. In contrast, for non-adsorbing compounds, a wide range of rejection was seen as a function of flux. That means, at low TMF the diffusive flux is large compared to the water flux whereas at high TMF the diffusive flux is low compared to water flux. For the well rejected larger DBPs only a small impact of flux on rejection was observed for both NF and RO membranes. Doederer et al. (2014) and Kong et al. 2016) showed a great dependence of rejection on applied pressure (and water flux) and, hence, at higher pressure a higher rejection of hormonally active agents and PhACs was observed both for the HL and NF270 membranes tested. The impact of pressure on rejection was greater for hormonally active agents than for PhACs since hormonally active agents are of smaller MW than the PhACs examined in the study (Kong et al. 2016).

1.3.4.2 Cross-flow velocity/recovery/concentration polarisation

Cross flow filtration is a very common type of filtration in the purification of water. It is characterised by a tangential flow of the feed across the membrane surface being able to

wash away rejected solutes and particles. The velocity of this tangential flow may substantially impact the filtration process (Drazevic et al. 2014). NF/RO are pressure and concentration driven processes so enhanced concentrations at the membrane surface may significantly affect the membrane performance, namely flux reduction and solute removal (Bouchoux et al. 2005, Déon et al. 2013).

Hydrodynamic conditions (cross-flow velocity, CFV) and the resulting concentration polarisation phenomena may significantly affect water permeability and removal of organic solutes in cross-flow NF, hence making them important optimisation parameters (Drazevic et al. 2014). The authors observed that a change in CFV affected rejection of small solutes a lot more than that of larger solutes, which is due to low friction between the pore wall and small solutes leading to a high solute flux. This, in turn, results in a high sensitivity to changes in solute concentration at the membrane surface. In contrast; for large solutes friction between the pore wall and solute is high resulting in a low solute flux and consequently in a low sensitivity to changes in solute concentration at the membrane surface. This observation was confirmed by Doederer et al. (2014) who did not see an effect of changing CFV on rejection of larger molecules and adsorbing solutes (THMs). In general, there was no discernable impact on rejection of DBPs for an NF membrane when CFV was varied apart from a slight increase of rejection for dihaloacetonitriles (DHANs) (8 to 11%) when CFV was 4 times higher. The underlining mechanisms of the observations are the reduction of the concentration polarisation layer by the increase of CFV. The adsorbing solutes interact with the membrane material inside the active layer of the membrane so they are not affected by changes to the concentration polarisation layer induced by increased turbulence with increased CFV.

A decrease of rejection with increasing recovery was reported in the literature (Fujioka et al. 2014b, Verliefde et al. 2009). This is due to an accumulation of rejected solutes toward the exit of the feed stream. With a simultaneous reduction of the cross-flow velocity in order to increase recovery concentration polarisation increases towards the tail-end particularly of the last stage of a membrane skid.

1.3.5 Impact of fouling on rejection

The prevention of fouling remains an unsolved problem in membrane water treatment applications resulting in high operational costs and low product efficiency (Lee et al. 2016).

There are four basic types of fouling, namely organic, colloidal, inorganic and biological fouling. Under fouling conditions, membrane rejection behaviour of small organic solutes is particularly complex and rejection predictions are difficult. This is underlined by often contrary observations, i.e. decrease (Verliefde et al. 2013, Xu et al. 2006a) as well as increase (Schäfer et al. 2002, Verliefde et al. 2009, Yangali-Quintanilla et al. 2009) in rejection of TrOCs by fouled membranes. Mahlangu et al. (2016) have listed several factors/interactions potentially impacting on rejection of TrOCs by a fouled membrane:

1. Adsorption of the organics onto foulant molecules or the fouling layer leads to an improved rejection due to hindered partitioning and diffusion across the membrane (Schäfer et al. 2003, Yangali-Quintanilla et al. 2009). Interaction of the solutes and NOM may be governed by the formation of hydrogen bonds, van der Waals interactions and dielectric interactions (Neale et al. 2008);
2. Hindered back-diffusion of the trace organics in the fouling layer may lead to cake-enhanced concentration polarisation. An increased concentration gradient of the solutes between the feed and permeate side of the membrane results in an increased partitioning of the organics into the membrane, and transport to the permeate side, effecting in lower rejections (Lee et al. 2006, Lee et al. 2004, Yangali-Quintanilla et al. 2009);
3. Changing membrane surface characteristics impact trace organics transport: enhanced sieving effects (due to pore blocking/pore constriction), increased/decreased electrostatic effects (due to different surface charge characteristics of membrane and fouling layer), and non-electrostatic, affinity interactions will be subject to change due to the altering of the membrane surface properties.
4. The impact of flux reduction, considered as one of the major implications of fouling, on rejection of organic solutes has often been overlooked in previous studies. (Boussu et al. 2006, Hajibabania et al. 2011, Paul 2004, Verliefde et al. 2009). The solution-diffusion model shows a direct proportionality between flux and solute rejection so an observed decrease in rejection might be solely due to a decrease in flux. Hence, a flux correction of rejection data might reveal an observation in a different light. The authors concluded to compare trace organic rejection of fouled and unfouled membranes at the same flux in order to determine the real implications of fouling on solute rejection.

Studies published in literature often do not only deal with single foulants but rather combine foulants out of the four types of fouling described above. This combined fouling will be described within the following sections where applicable.

1.3.5.1 Organic fouling

In this section, the implications of organic fouling on NF/RO membrane filtration will be discussed. Studies were carried out with secondary or tertiary treated wastewater (Azais et al. 2014, Azaïs et al. 2016, Fujioka et al. 2013a, Simon et al. 2013b), synthetic wastewater/foulants (Azaïs et al. 2016, Fujioka et al. 2013a, Simon et al. 2013b), in the presence and absence of divalent ions such as Ca^{2+} (Azaïs et al. 2016, Mahlangu et al. 2014a), and considering combined fouling (Mahlangu et al. 2014a).

Feng et al. (2015) carried out fouling tests with NF membranes which were fouled with algogenic organic matter (AOM). Fouling enhanced naproxen removal due to extended charge repulsion, since the surface of the fouling layer is more negatively charged. Hence, with increasing fouling layer thickness the interaction changes from naproxen-membrane over to naproxen-fouling layer. Similar results, i.e. surface properties such as charge (Azais et al. 2014) and hydrophobicity (Azais et al. 2014, Bellona et al. 2010, Comerton et al. 2009, Mahlangu et al. 2014a) of a fouled membrane are determined by the overlaying fouling layer were reported in literature.

In accordance with Feng et al. (2014), an increase in rejection (20%) for NDMA was observed for a membrane fouled by bulk organic matter from an MF permeate compared to the clean solution (Fujioka et al. 2014c). Simon et al. (2013b) studied organic fouling by synthetic wastewater and secondary effluent for the NF270 membrane and attributed the observed considerable increase in carbamazepine rejection to pore blocking. Azais et al. (2014, 2016) also observed an increase in rejection both for a loose (NF270) and a tight (NF90) NF membrane when filtering membrane bioreactor (MBR) effluent. These results were explained by the association of organic macromolecules with the PhACs (solute-solute interaction) forming complexes, which in turn were leading to an additional sieving effect or charge repulsion (solute-membrane interaction). PhAC-EfOM complexation leading to an enhanced size and hence better rejection was also observed in previous studies (Comerton et al. 2009, Sadmani et al. 2014). These mechanisms are thought to offset the simultaneously occurring CECP phenomenon and eventually resulting in a higher rejection. Additionally, this increase in rejection was higher for the loose NF270 than for the NF90 (Azais et al. 2014, Azaïs et al. 2016).

Azais et al. (2014) observed lower rejections for PhACs for pre-fouled (secondary effluent) NF270 membranes and attributed this to the cake-enhanced concentration polarisation effect. The results are consistent with previous observations from Kimura and co-authors

(Kimura et al. 2009), who concluded that the MBR process would be the favourable pre-treatment for NF/RO over the conventional activated sludge process followed by UF. The significance of CECP on solute rejection by relatively loose NF membranes such as the NF270 has also been pointed out for other TrOCs like pesticides (Plakas and Karabelas 2012).

Mahlangu et al. (2014a) conducted extensive fouling tests with carbamazepine for organic, colloidal, combined fouling, and the presence or absence of Ca^{2+} as well as comparisons with modelling results using the NF270 membrane (Mahlangu et al. 2014a). In general, fouling (organic, colloidal and combined fouling) altered the performance of NF270 membranes in terms of permeate flux and carbamazepine rejection. Fouling by alginate and Al_2O_3 led to carbamazepine rejection below that predicted by the solution-diffusion model but fitted predicted rejections by the cake-enhanced concentration polarisation model except in the presence of Ca^{2+} ions. This is seen as evidence of CECP. In contrast, no CECP effect was observed for combined fouling by Al_2O_3 + alginate (regardless of the presence of Ca^{2+}) due to the formation of dense "separating" layers that reject carbamazepine. The strong impact of the presence of Ca^{2+} ions (0.5 mM) on carbamazepine rejection was shown in alginate fouling tests. For example, rejection seems to or really declines in the absence of calcium ions by 70% over time, whereas with Ca^{2+} in the feed solution a 13 % rejection decline was observed, when not flux corrected. After flux correction, the apparent rejection decline for carbamazepine turns into an increase in rejection. According to the authors, flux and CECP were not the only factors explaining rejection, but also hydrophobic interactions between solute and membrane were effective. The membrane hydrophobicity increased due to fouling and hence one would expect higher solute-membrane interactions between the slightly hydrophobic carbamazepine and the membrane. Enhanced non-electrostatic solute-membrane affinity could lead to an increase in the partitioning of carbamazepine into the foulant/membrane matrix and thus result in a decrease in overall rejection of carbamazepine. This mechanism has been previously reported (Verliefde et al. 2007a). In contrast to the study described above (Mahlangu et al. 2014a), Azais et al. (2016) conducted experiments using more realistic and therefore higher feed calcium concentrations (8 mM), which led to a diffuse and solute-permeable fouling layer. A lower rejection for the neutral TrOCs was observed, which was attributed to a preferential reaction of EfOM and calcium leaving a larger proportion of TrOCs uncomplexed than in the absence of calcium in the feed.

As noted in section 1.3.5, Mahlangu et al. (2014a) stated an important finding that some foulants improve solute rejection performance of the membrane when compared to the results of the clean membrane at the same flux (Mahlangu et al. 2014a). Hence, comparisons of rejection values of fouled membrane vs. clean membranes should always be undertaken at similar flux values, which is in accordance with the findings reported by Azais et al. (2016).

1.3.5.2 Colloidal fouling

As already discussed in the previous section Mahlangu et al. (2014a) have also extensively studied colloidal fouling, again in the absence or presence of Ca^{2+}, and its impact on the rejection of TrOCs by the NF270 membrane. A decline in carbamazepine rejection was observed when the membrane was fouled with colloidal latex in the presence (20%) and absence (41%) of 0.5 mM Ca^{2+}. However, after flux correction, the decrease turned into an increase in real rejection! It is reported that the addition of $CaCl_2$ altered the fouling layer and thereby reduced CECP effects, which in turn resulted in clearly less decline (not flux corrected) in rejection of carbamazepine. For the other colloidal foulant tested, namely Al_2O_3, a similar decline of the carbamazepine rejection was observed although latex caused clearly more flux decline than the aluminium oxide. For pure Al_2O_3 fouling, there could be CECP, but as soon as alginate and particularly when alginate and Ca^{2+} are present, carbamazepine rejection significantly declines less as compared to the CECP model. Therefore, not CECP, but the formation of a dense layer is governing rejection, which means the effect of solute-membrane affinity becomes the dominant rejection mechanism.

Since there was no significant change of the membrane hydrophobicity when fouled by Al_2O_3, non-electrostatic affinity interactions would not be expected to play a major role, Al_2O_3 membrane fouling exerts on the rejection of carbamazepine. However, there are other inter-molecular interactions existing in addition to hydrophobic-hydrophobic interactions. Accordingly, Mahlangu et al. (2014a) suggest to correlate trends in rejection to solute-membrane interaction energy and not just the contact angle with water. Attractive/repulsive forces are describable by the determination of interfacial free energy. After fouling (all types incl. combinations) interfacial free energy IFE is negative, which leads to an attraction of carbamazepine to the fouling layer. This results in more partitioning of

carbamazepine onto the fouled membrane surface due to increased affinity, eventually causing a reduced carbamazepine rejection.

In another investigation, Mahlangu et al. (2014b) studied the impact of colloidal fouling (latex) on NF performance. Regardless of the presence of Ca^{2+}, colloidal fouling did not influence the rejection behaviour of caffeine by the NF membrane. However, a minor increase in rejection in the absence of Ca^{2+} due to the formation of an active latex layer was observed. Flux corrected, a significantly improved caffeine rejection by the membrane fouled with latex was revealed compared to the rejection by a virgin membrane at similar fluxes. According to the authors of the study, these findings show the need for a pre-treatment prior to NF to avoid or reduce fouling. Additionally, membranes with better anti-fouling properties are necessary.

Lin et al. (2014) studied the effects of silica fouling on the removal of PPCPs by NF/RO. Adsorption of ibuprofen, triclosan, and sulfamethoxazole as well a more hydrophilic membrane surface were observed. Furthermore, silica fouling on tight membranes (NF90 and XLE) was able to improve the rejection of most PPCPs due to a dense fouling layer facilitating a synergistic steric hindrance by the fouled membrane. Therefore, transport of PPCPs across the membrane surface was reduced, implying that size exclusion was the dominating rejection mechanism.

1.3.5.3 Inorganic fouling (scaling)

During the filtration process with NF/RO membranes – depending on the composition of the feed solution – the concentration of various marginally soluble divalent and multivalent salts may increase near the membrane surface due to their rejection by the NF/RO membrane (Shenvi et al. 2015). At the stage of supersaturation, i.e. when the solubility limit is exceeded these salts precipitate resulting in the formation of a scaling layer on the membrane surface (Hasson et al. 2001). Typical scale forming salts include barium sulfate, calcium carbonate, calcium sulfate, silica and ion salts. Anti-scalants addition is a widely accepted method to prevent scaling by increasing the threshold for the onset of scale formation (Semiat et al. 2003).

There has been very limited research on the impact of scaling on TrOCs rejection. Scaling, if not mitigated, often leads to complete loss of flux. Hence, the impact on TrOC rejection becomes irrelevant. In chapter 4, a study on combined organic and inorganic fouling and

its impact on the rejection of TrOCs on a lab-scale basis and simulating a worst case scenario is presented.

1.3.5.4 Biological fouling

Garcia-Vaquero et al. studied drinking water treatment by NF using a conventionally treated surface water as feed (Garcia-Vaquero et al. 2014). According to the authors, reservoir water has a strong hydrophilic composition due to protein-like substances that can promote biofouling. The NF membranes effectively removed the hydrophobic fraction (66%) whereas the hydrophilic fraction remained in the permeate. The latter fraction tends to promote biofouling so the biofouling propensity was not eliminated by rejection of a large proportion of the hydrophobic fraction.

Similar to inorganic fouling (scaling), as noted in section 1.3.5.3, research on the impact of biofouling on the rejection of TrOCs is also very limited. This is largely due to the extensive effort that needs to be taken to simulate biological fouling.

1.3.6 Impact of membrane cleaning on rejection

As discussed in the previous section membrane fouling remains an inseparable part of membrane filtration processes. The outcome of this is the necessity of membrane cleaning. For a cleaning procedure, suitable cleaning agents are often combined or applied subsequently to restore the membrane performance. Commonly used membrane cleaning reagents include acidic, caustic, surfactants and metal chelating reagents (Simon et al. 2013a). Cleaning reagents may affect membrane morphology as well as the rejection of TrOCs, which will be discussed in the sections below.

1.3.6.1 Changes of membrane morphology due to cleaning

Simon & Nghiem (2014) have undertaken extensive studies on the implications of membrane cleaning on the membrane morphology. Scanning electron microscope-electron dispersive spectroscopy (SEM-EDS) analysis demonstrated the presence of chlorine within

the membrane polymeric matrix after being exposed to hypochlorite. It was shown that membrane chlorination leads to a destruction of hydrogen bonds of C=O and N-H groups. Interestingly, both an increase and a decrease of the contact angle were observed, depending on the hypochlorite concentration. A low concentration (100 mg/L hypochlorite) led to a large increase in the hydrophobicity, while at 2,000 mg/L hypochlorite hydrophobicity tended to decrease. The authors proposed two respective mechanisms underlining the influence of chlorination on membrane hydrophobicity. Firstly, at a low chlorine concentration, N-chlorination occurs resulting in a reduction of the hydrogen bonding sites. And secondly, the exposure of the membrane to high chlorine concentrations may lead to the presence of unbalanced dipole moments and/or the dissolution of the coating layer. Additionally, a considerable decrease of the surface roughness after hypochlorite treatment was observed, which was attributed to the conformational rearrangement of the polymeric chains of the polyamide active skin layer. It was concluded that changes in membrane surface morphology are likely to be affected by various structural parameters including thickness and actual chemical composition of the polyamide skin layer (Simon and Nghiem 2014).

Simon et al (2013a) also examined the impact of caustic cleaning agents on permeability, which increased significantly (NF270) and slightly (NF90), respectively. This was caused by an increase in average pore radius for the NF270 due to the high pH. That leads to a further deprotonation of the functional groups (COOH and NH) resulting in more negative charge moieties in the active skin layer of the membrane. Consequently, conformational rearrangements of the polyamide structure occur leading to an increase in pore size. Simon et al. (2009) reported a considerable increase in permeability due to hysteresis, particularly when the membrane has a very thin active skin layer. For the NF90 membrane, an increase in surface hydrophilicity was observed.

1.3.6.2 Impact on rejection of TrOCs due to cleaning

The impact of membrane cleaning on the rejection of TrOCs had been largely overlooked until Simon & Nghiem (2014) conducted several comprehensive studies and shed light on this important field of membrane research. So they observed a small increase in sulfamethoxazole rejection by all four membranes tested after they had been exposed to a low concentration (100 mg/L) of hypochlorite. This observation was attributed to a “tight-

ening up effect" previously proposed by Kang and co-authors (Kang et al. 2007). Additionally, exposure to hypochlorite led to a significant increase in the membrane charge density (Simon et al. 2009). Hence, charge repulsion is enhanced as well, which consequently results in an increase in rejection of negatively charged solutes (Simon and Nghiem 2014). When exposing the membrane to a higher concentration of hypochlorite (2,000 mg/L) a detrimental effect on the membrane separation capacity was proposed since the membrane showed a considerable decrease in rejection over filtration time. This was assumed to be due to a possible rearrangement of the polyamide chains under the influence of chlorine degradation and filtration pressure. It was shown that both the positive and negative impact of hypochlorite exposure was more significant for the neutral carbamazepine than that of the negatively charged sulfamethoxazole. According to the results obtained the loose nanofiltration membrane NF270 exerts a higher sensitivity to chlorine exposure than the other tight NF and the two RO membranes tested (Simon and Nghiem 2014).

Simon et al (2013a) also conducted a study on the impact of caustic cleaning formulations (CCFs) on the rejection of three groups of TrOCs, namely neutral hydrophilic, neutral hydrophobic, and negatively charged compounds. A significant decrease in the rejection of neutral hydrophilic TrOCs was observed for the NF270 membrane. The membrane's high sensitivity to caustic cleaning was attributed to its very thin and loose active skin layer. In contrast, caustic cleaning did not affect the pore size of the NF90 membrane due to the thicker active skin layer. Hence there was no impact on rejection of TrOCs for the NF90. Out of the three groups tested, neutral hydrophobic TrOCs were the most significantly affected group by caustic cleaning. Initially, a strong adsorption to the membrane occurred, whereas after 24 h rejection was predominantly controlled by size exclusion. In addition, the rate of adsorption and the total possible mass adsorption of TrOCs to the membrane matrix is affected by the increase of hydrophilicity and/or pore size. Consequently, this leads to enhanced diffusion of hydrophobic TrOCs. For the negatively charged TrOCs, the impact of caustic cleaning was least pronounced out of the three groups of compounds tested. A small but discernible decrease in rejection was observed after exposure of the NF270 membrane to CCFs. This variation is predominantly attributed to enlargement of the membrane pore size. There was no discernible impact of caustic cleaning on the charge for the NF270 and the NF90. Furthermore, caustic cleaning did not affect the rejection for the NF90 membrane which is consistent with the impact of caustic cleaning on the pore size (Simon et al. 2013a).

Another study by Simon et al. (2013b) dealt with fouling and cleaning tests. A slight increase of the rejection of SMX due to fouling was observed. Further successive fouling and caustic cleaning did not significantly influence SMX rejection due to charge repulsion being the predominant rejection mechanism. Hence, the impact of pore enlargement was minimal. The observed permanent increase in SMX rejection was probably due to the adsorption of negatively charged foulants to the membrane polymer. An interesting observation was the fact that cleaning could not recover the membrane charge and hydrophobicity to the state of the virgin membrane. For carbamazepine the impact of two repetitive fouling-cleaning cycles on rejection was different. This was presumed to be due to a progressive modification of the membrane surface, i.e. adsorption of negatively charged and hydrophobic foulants and/or an escalating impact of caustic cleaning on the membrane polymer (Simon et al. 2013b). According to (Simon et al. 2013c) the severe decrease in rejection of CBZ might not be permanent. It was shown that a dual step cleaning (caustic followed by acidic cleaning) may be applied in order to minimise the impact of caustic cleaning.

1.3.7 Validation at pilot and full scale systems

Comparing the number of studies on the rejection of TrOCs by NF/RO during 2014 and 2016 overwhelmingly shows the prevalence of lab-scale over pilot-scale studies. This is clearly demonstrated in Figure 1-3.

Bellona et al. (2012) noted the limitations of bench-scale studies, often using flat-sheet or dead-end filtration cells. It was suggested to perform long-term investigations at pilot-scale using spiral wound membrane elements with real feed water available at a full-scale water reuse facility. Results from Fujioka et al. (2014c) show differences in rejection of N-nitrosamines between lab-scale study (flat sheet membranes) and pilot-scale study (spiral wound membranes). Rejections at pilot-scale were lower due to a significantly higher system recovery used on pilot-scale, which is in accordance with Fujioka et al. (2015b) and Verliefde et al. (2009). The impact of recovery was discussed in section 1.3.4.2.

Consequently, there is a need for more pilot-scale or even full-scale testing in order to overcome the abovementioned limitations of bench-scale studies and produce reliable data that represent real live conditions of full-scale applications.

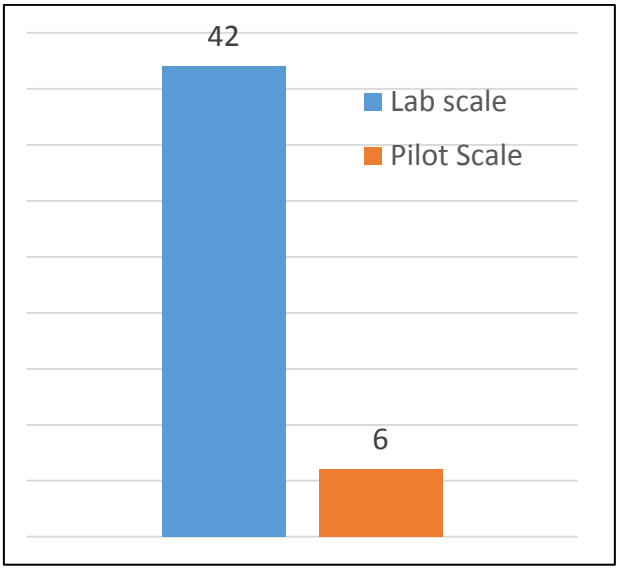


Figure 1-3: Numbers of studies with regard to TrOCs removal by NF/RO conducted on lab scale vs. pilot scale between 2014 and 2016 (total number of studies = 48)

2 Membrane fouling in the nanofiltration of landfill leachate and its impact on trace contaminant removal

2.1 Introduction

Waste generation and hence its management have been part of human existence on earth for thousands of years. Landfilling, i.e. disposal of the waste on or beneath the ground, has, for several reasons, been the most widespread method of waste management worldwide. Although alternative disposal technologies, such as incineration, are fully developed, to date, higher cost and limited capacities of those alternatives have led to an unbroken popularity of landfilling. In Australia, landfilling is the most common method of waste disposal and solid waste from almost all streams i.e. municipal, commercial and industrial, construction and demolition, as well as controlled waste, are disposed of in landfills (Newton et al. 2001). In 1996/97, a total amount of 21.2 million tonnes of solid waste was sent to landfills, corresponding to a per capita disposal rate of more than 1.1 tonnes per annum. More than 95% of the total solid waste generated was received by landfills in some states and territories in 2001 (Newton et al. 2001). While there has been a considerable increase in recycling and waste diversion activities, this positive outcome has been offset by a steady increase in population.

Beside the emission of landfill gas, the release of leachate is the major route of interaction of a landfill with the environment and therefore is considered to pose the greatest potential for environmental harm (Christensen et al. 1989). Leachate is predominantly generated from precipitation onto the landfill surface, the moisture of the waste itself and, to a limited extent, groundwater (if the bottom of the landfill is not lined) or other water infiltration (Bilitewski et al. 1997). During the percolation through the body of the landfill, the infiltrated water is severely contaminated with a complex mixture of organic and inorganic contaminants. Therefore, leachate collection followed by an adequate treatment process is important for the protection of surface and subsurface watercourses and, depending on legislation, required in many countries (Anonymous 1999).

According to Bilitewski et al. (1997) all contaminated water that has been in contact with waste is defined as leachate. Its formation is the result of complex hydrodynamic and physico-chemical processes within the landfill body. The expected quantity and quality of the leachate depends on a number of factors, e.g. climate, moisture content of the waste, landfill operation, and landfill age. Within the landfill, water can be stored by the waste and due to biochemical processes water is mostly consumed since they mainly proceed

under anaerobic conditions (Bilitewski et al. 1997, Melin et al. 2005). Guideline figures for leachate generation of 31 to 58% of the precipitation were reported for landfills with unconsolidated surface and 25 to 40% of the precipitation for landfills with compacted surface (Bilitewski et al. 1997).

Apart from the factors mentioned above, the characteristics of landfill leachate also depend on a number of other parameters, such as waste composition, the biochemical decomposition of the waste within the landfill, its pH range, and the amount of water retained (Bilitewski et al. 1997). Thus, the leachate composition varies significantly among landfills. Leachate from municipal landfills typically contains 0.2 to 1.5% solutes, of which the largest portion (80 to 95 wt%) consists of monovalent salts (Dahm et al. 1994). Furthermore, leachate may contain a large amount of inorganic nitrogen compounds, mainly as ammonia. A small portion (approximately up to 1 g/L) of the inorganic contents of leachate is made up by heavy metals. The remaining 5 to 20 wt% are made up of organic compounds. Christensen et al. (1989) classified leachate pollutants from a typical landfill receiving municipal and commercial wastes (not industrial waste) into four groups: (1) Common inorganic cations and anions; (2) Heavy metals; (3) Organic matter; and (4) Specific organic compounds (originating from household or industrial chemicals, present in relatively low concentrations, usually less than 100 µg/L). In particular, the occurrence of these specific organic compounds of the last group at trace level has attracted many intensive research efforts over the last decade. These studies revealed that an extensive range of organic compounds such as plasticisers (phthalates), pesticides, pharmaceuticals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, flame retardants can be found ubiquitously in landfill leachate (Behnisch et al. 2001, Paxéus 2000, Yamamoto and Yasuhara 1999). This, once again, underlines the necessity of sufficient treatment of the leachate to avoid negative environmental impact.

Most Australian landfills currently have an onsite pre-treatment process to reduce ammonia prior to sewer disposal as trade waste. However, as landfills are being located further away from metropolitan areas and sewage treatment plants, it would be more cost-effective to have direct leachate disposal after being treated by advanced treatment processes, which can meet the very stringent discharge regulations required. In fact, this has been proven to be an effective approach in Europe, particularly in Germany. Amongst several technologies currently available for the treatment of landfill leachate, nanofiltration has

emerged as an attractive option since complementary combinations with pre-/post-treatment can be more cost-effective than the reverse osmosis applications that are most commonly used at present (Melin et al. 2005).

However, NF is not suitable as a single process in landfill leachate treatment since it has a low rejection for nitrogen compounds (Trebouet et al. 2001) and can be subjected to severe fouling. Hence, combined processes are used in full-scale applications. These basically contain a biological treatment (conventional nitrification/denitrification or sequencing batch reactor combined with sedimentation tank or ultrafiltration membrane for sludge retention) followed by the NF stage. However, it must be pointed out that for landfill leachate even a very comprehensive pre-treatment will not be able to completely eliminate potential fouling causing constituents. Thus, fouling will always be a part of membrane applications in the treatment of polluted water.

Membrane fouling can be defined as irreversible flux decline (and thus loss of performance), which can only be removed by physical and chemical cleaning. Fouling in NF is a very important factor due to its negative impact on the competitiveness of the process. Generally fouling can be categorised as organic, inorganic, particulate, and biological fouling (Schäfer et al. 2005). Depending on the pre-treatment, organic and inorganic fouling probably exhibit the most significant impact on the application of NF for landfill leachate treatment, for which the fouling potential has been found to be high, reflected by the fouling index ranging between 3.5 and 5.4 (Trebouet et al. 1999). Due to the high concentrations of organic matter in landfill leachate, organic fouling is expected to play a major role in membrane filtration (Scott et al. 2005). Despite the high fouling propensity of leachate, the effects of membrane fouling on rejection in the nanofiltration process of landfill leachate have, to date, been largely overlooked. In fact, several studies investigating the nanofiltration of groundwater and secondary effluent have revealed some considerable effects of membrane fouling on the rejection of organic contaminants (Xu et al. 2006a). These authors attributed the differences in the rejection between virgin and (organically) fouled NF membranes to the changed membrane characteristics. Nghiem et al. (2002) reported a decrease in the rejection of the trace organic compound estrone when the feed water contained natural organic matter compared to pure Milli-Q water. In other more recent studies, some observable effects of organic matter on the rejection of several herbicides (Plakas et al. 2006) and on the membrane characteristics (Xu et al. 2006a) have been reported. Furthermore, Plakas et al. (2006) suggested that the extent of membrane foul-

ing as well as the structure of the foulants and solutes might have an influence on rejection. Calcium was shown to affect rejection of herbicides differently depending on whether it was applied alone or in conjunction with organic matter. While most of these findings to some degree demonstrate the importance of the feed water constituents in membrane filtration processes, the underlying mechanisms governing membrane fouling and especially the influence of fouling on trace organic rejection remain unclear.

In this study, the effects of natural organic matter in combination with calcium on the fouling behaviour of NF membranes were investigated using a synthetic landfill leachate. Bisphenol A (BPA), which is found ubiquitously in landfill leachate and is also one of the most significant endocrine disrupting chemicals, was selected as a model trace organic compound. Membrane filtration experiments were conducted under accelerated fouling conditions, thus, enabling a detailed examination of the fouling behaviour during landfill leachate nanofiltration processes. The influence of fouling on the rejection of BPA and possible mechanisms were also delineated and discussed.

2.2 Materials and Methods

2.2.1 Analytical reagents and chemicals

All chemicals used in this investigation were of analytical grade and supplied by APS Australia, Auburn, NSW, Australia unless otherwise stated. Chemical solutions and feed waters were prepared with deionized (DI) water (Milli-Q Ultra Pure Water System, Millipore, North Ryde, NSW, Australia). Adjustments of the pH value were carried out using 1 M sodium hydroxide (NaOH) or 1 M hydrochloric acid (HCl), respectively. A stock solution (1 g/L) of bisphenol A (Sigma Aldrich, Castle Hill, NSW, Australia) was prepared in pure methanol (HPLC grade). It was stored in the freezer at -4 °C and used within 1 month.

2.2.2 Nanofiltration membrane

A commercially available NF membrane, namely NF270 (FilmTec Corp., Minneapolis, MN, USA), was used in this study. The membrane was received as flat sheet and was stored under dry conditions at room temperature. According to the manufacturer, the membrane is thin-film composite with a polyamide active layer on a microporous polysulfone supporting layer.

2.2.3 Membrane filtration set-up and protocol

A laboratory-scale crossflow NF set-up (Figure 2-1) was used in this study. The NF/RO filtration unit comprises a stainless steel plate-and-frame membrane cell with an effective surface area of 7.7 cm x 3.0 cm, a 15 L stainless steel feed tank, and a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN, USA). Retentate flow rate was monitored by a rotameter. Feed pressure and crossflow velocity were controlled by means of a bypass valve and a back pressure regulator.

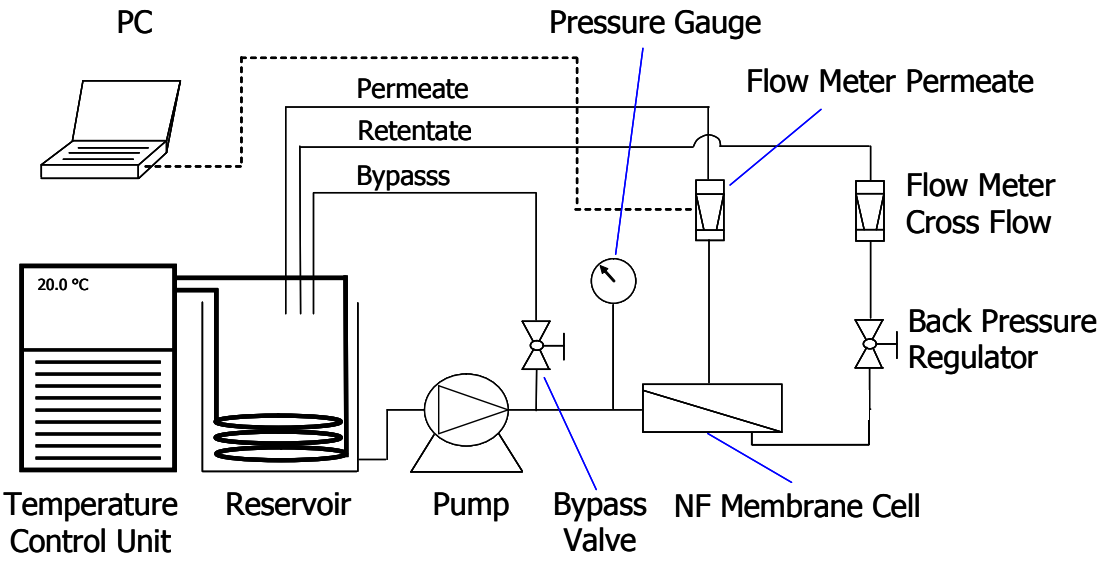


Figure 2-1: Schematic diagram of the laboratory-scale cross-flow nanofiltration test unit

Prior to every membrane filtration test two consecutive pre-treatment steps were carried out. Firstly, a membrane compaction was performed at a feed pressure of 130 kPa for 1 h using DI water in the feed tank. Then a fouling cocktail containing $NaHCO_3$, NaCl and humic acid was added to make up concentrations of 1 mM, 20 mM and 20 mg/L in the feed water (total volume = 7 L), respectively. Depending on the experiment, the concentration of $CaCl_2$ was set to 0, 0.5, 1 or 4 mM/L in the feed solution. Subsequently, the fouling layer was established on the membrane surface by running the system at a pressure of 1000 kPa for 18 h. Throughout the experiment, the permeate was recycled back to the feed tank after passing through a digital flow meter (Optiflow 1000, J&W Humonics, Folsom, CA, USA), connected to a PC, to monitor the flow rate. All experiments were run at a cross-flow rate of 30.4 cm/s and a constant temperature of the feed solution of 20 ±0.5 °C,

controlled by a circulating heater/chiller (Neslab RTE 7, Newington, NH, USA). A digital pH meter (Model 744, Metrohm, Herisau, Switzerland) was used for the measurements of pH.

After the fouling development, the permeate flow rate was set to 3.7 mL/min followed by the addition of BPA to make up a concentration of 750 µg/L in the feed solution. Samples of feed and permeate (approximately 1.5 mL) were collected at specified intervals.

2.2.4 Analytical technique

A Shimadzu high-performance liquid chromatography (HPLC, Rydalmere, NSW, Australia) system was used to analyse the organic contaminant bisphenol A. The solvent delivery system included two HPLC pumps, a degaser, and a gradient mixer. A reversed phase column (Discovery® C18 with particle size, length, and diameter of 5 µm, 250 mm, and 4.6 mm, respectively) supplied by Supelco (Castle Hill, NSW, Australia) was used. The UV wavelength was set at 280 nm. Premixed mobile phase was prepared using HPLC grade Acetonitrile (ACN) and an aqueous buffer solution (DI water containing 25 mmol/l of KH_2PO_4): Eluent A (80% ACN/20% aqueous buffer solution) and eluent B (20% ACN/80% aqueous buffer solution). Further details of this analysis method are available elsewhere (Nghiem et al. 2005b).

2.3 Results and discussion

2.3.1 Landfill leachate characterisation

A literature review was conducted to examine the typical compositions of the major constituents in landfill leachate. The results are summarised in Table 2-1, which clearly highlights the elevated salt concentrations and dissolved organic matter as the major constituents in landfill leachate. Furthermore, it is interesting to note that all parameters are subject to large variations, approximately 3 orders of magnitude or more. As a result of this literature review study, a model synthetic landfill leachate was selected to present the characteristics typical to those of real leachate (Table 2-1).

Table 2-1: Concentrations of salts and dissolved organic carbon in typical landfill leachate and composition of the synthetic leachate solution used in this study.

Parameter	Real Landfill Leachate Concentration	HA Content as part of DOC		References	**Synthetic Landfill Leachate**
	mg/L	%	mg/L		**mg/L**
Sodium	2,770			Xu, Y.-D. et al. (2006b)	**483**
	0-8,000			Scott et al.(2005)	
Calcium	38			Xu, Y.-D. et al. (2006b)	**0, 20, 40, 160[1]**
	4-7,200			Scott et al.(2005)	
Chloride	34-11,375			Scott et al.(2005)	**780**
DOC	649	4	26	Xu, Y.-D. et al. (2006b)	**6[2]**
	78 - 663			Choi and Lee (2006)	
	Average (n=5) = 388				
	57 - 138			Nanny and Ratasuk (2002)	
	Average (n=3) = 89				
		4-44		Artiola-Fortuny and Fuller (1982), Castagnoli et al.(1990)	
		10		Christensen et al.(1998)	

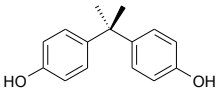
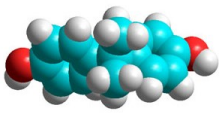
[1] depending on the experiment

[2] 20 mg/L HA added to feed water

2.3.2 Physico-chemical properties of bisphenol A

Important physico-chemical and toxicological properties of BPA are presented in Table 2-2. BPA has a moderately high octanol-water partitioning coefficient (log K_{OW}) which indicates the hydrophobicity of the compound leading to an instant adsorption to hydrophobic materials. BPA is a weak acid with the two phenolic groups having a pK_a value of 10.1. That means that at the pH value present during the experiments (approximately 8.1), the functional groups are not dissociated so the compound remains neutral.

Table 2-2: Physico-chemical and toxicological characteristics of Bisphenol A (BPA)

Formula	$C_{15}H_{16}O_2$	Chemical Structure
MW (g/mol)	228	 
Solubility in Water (mg/L)	129	
pK_a	10.1	
Log K_{ow}	3.32	

2.3.3 Influence of the calcium concentration on the flux

A clear impact of the feed water calcium concentration on the flux was found in this study. Figure 2-2 shows the normalised flux profiles over time during the fouling layer development phase (18 h) for 4 different calcium concentrations in the feed water. All curves show a relatively similar profile with an initial steep drop followed by a delayed flux decline over time.

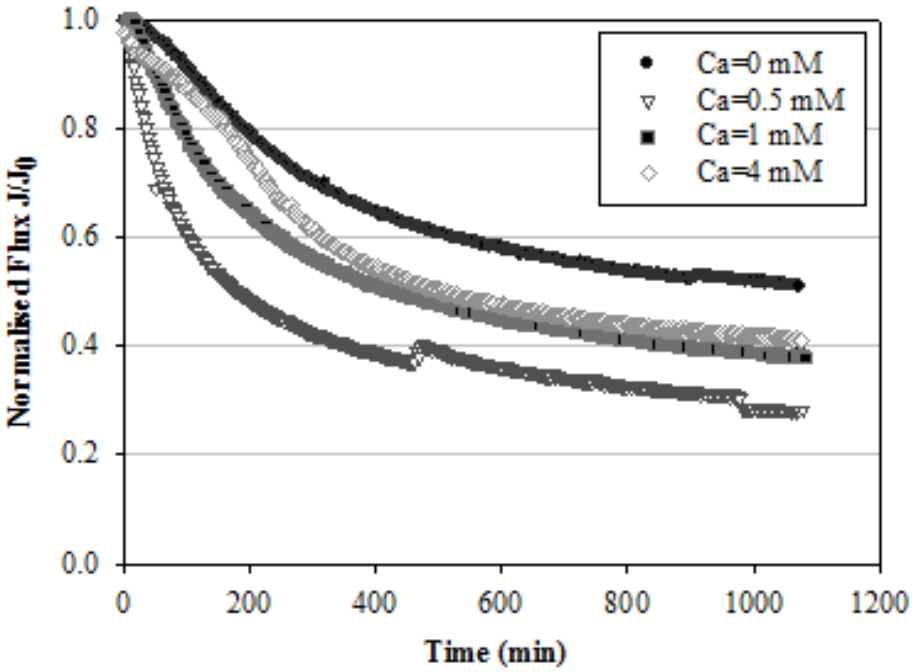


Figure 2-2: Influence of feed solution calcium concentration on permeate flux. The feed solution contained 750 µg/L of BPA, 1 mM of $NaHCO_3$, 20 mM of NaCl, 20 mg/L of humic acid and variable calcium concentrations, pH = 8.

As expected, the flux decline over time was lowest when no calcium was present. It dropped to 52 % of the initial value after 18 h, which can be attributed solely to organic fouling due to the humic acid in the feed solution (see Figure 2-3). Organic fouling is caused by the adsorption or deposition of organic matter to or on the membrane surface, gel formation, or pore blocking (Schäfer et al. 2005). All of these mechanisms can occur at the same time. As a result, it may not be possible to determine the actual extent to which each mechanism contributes to the fouling process.

Fouling increased as calcium was introduced to the feed water. The result reported here is consistent with several previous studies, which have demonstrated an increase in membrane fouling in the presence of calcium (and other multivalent cations) (Hong and Elimelech 1997, Seidel and Elimelech 2002, Teixeira and Rosa 2006). Intermolecular bridging between organic foulants and the membrane may be caused by cations (Seidel and Elimelech 2002). Furthermore, positively charged calcium ions can form complexes with the functional groups of the humic acid (solute-solute interaction), resulting in a reduction of the interchain repulsion between the macromolecules of the humic acid and can lead to the formation of small and coiled macromolecules. In addition, the calcium ions partly neutralise the negative charge of the membrane causing an increase in interaction between the membrane and the humic acid molecules (Teixeira and Rosa 2006).

In this study a steep decrease of the curves for 0.5 and 1 mM of calcium was observed at the beginning of the run which was possibly caused by pore blocking. In contrast, the flux decreased more slowly in the absence of calcium. The flux decline over time slows down for all curves with the progress of the experiment and after approximately 500 min all curves run relatively parallel. It is assumed that this more gentle increase of fouling is attributed to a second fouling mechanism, namely the formation and compaction of the cake layer on the membrane surface after the pores have been blocked.

The overall extent of flux decline with time was dependant on calcium concentration as follows: 0.5 mM > 1 mM > 4 mM > 0 mM. Thus, 0.5 mM appears to be a critical concentration for fouling at the conditions given in this study. This is consistent with a previous study by Nghiem et al. (2006a) who reported a peak in membrane fouling in the ultrafiltration of greywater at a similar calcium concentration. It is hypothesised that a high calcium concentration may lead to the formation of large and compact aggregates (or flocs) that are bigger than the pores. Thus, they cannot penetrate into the membrane and cause pore blocking. Additionally, the cake layer formed may be more porous. This causes less hydraulic resistance and, consequently, a flux decline which is less severe. In contrast, at lower calcium concentrations, smaller aggregates are formed which has been shown for colloidal systems (Nghiem et al. 2006a). This results in a dense cake layer and/or pore blocking (Waite et al. 1999).

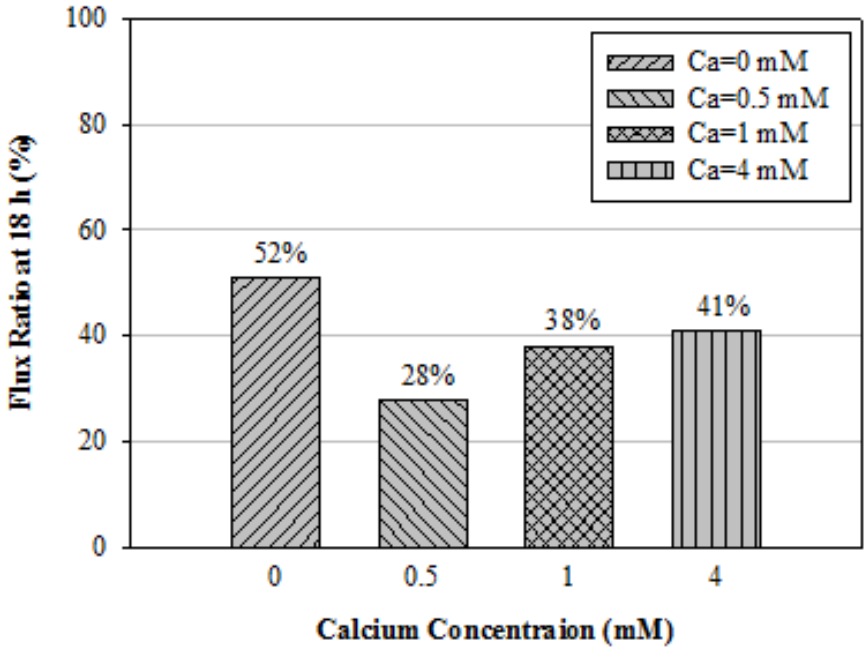


Figure 2-3: Permeate flux after 18 h of fouling layer development depending on calcium concentration in the feed water for a NF270 membrane. The feed water contained 750 µg/L of BPA, 1 mM of $NaHCO_3$, 20 mM of NaCl, 20 mg/L of humic acid and variable calcium concentrations, pH = 8.

2.3.4 Influence of fouling on the rejection of organic contaminants

Similar to the fouling studies, rejection tests with varying calcium concentrations were carried out. In Figure 2-4, BPA concentrations in the feed solution and the permeate as well as the rejection of BPA throughout the experiment are shown for a calcium concentration of 4 mM. The concentration of BPA in the feed water slowly decreases in the course of the run from approximately 750 to 700 µg/L. The permeate concentration increases sharply in the beginning of the test starting at approximately 75 µg/L. The curve starts to stabilise from ca. 70 min and reaches 490 µg/L at 120 min. After that only a very slight increase of the permeate BPA concentration was observed. Accordingly, the rejection shows a sharp decrease in the beginning of the test, starting at 90% and reaching an almost stable level of approximately 30% after 10 hours.

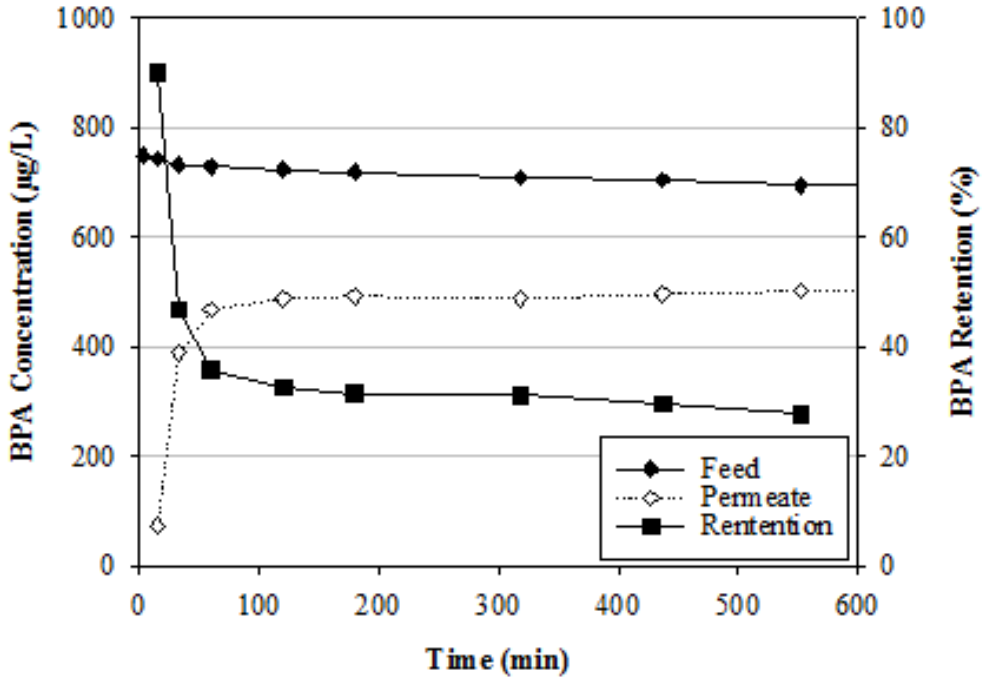


Figure 2-4: Concentrations of BPA in feed water and permeate and rejection of BPA for a calcium concentration of 4 mM in the feed water for a NF270 membrane. The feed water contained 750 µg/L of BPA, 1 mM of $NaHCO_3$, 20 mM of NaCl, 20 mg/L of humic acid, pH = 8.

An initial drop of the rejection of BPA was observed for all calcium concentrations (data shown for 4 mM of calcium only), however, the extent was different which eventually leads to quite significant differences in rejection of BPA as shown in Figure 2-5. Adsorption of BPA to the membrane surface and possibly the humic acid is responsible for the high rejection in the beginning of the test which is consistent with previous studies where a significant adsorption of hydrophobic, neutral compounds onto NF membranes was found (Kimura et al. 2003). Nghiem et al. (2005b) observed a similar initial drop of BPA rejection stabilising at approximately 45% rejection when running a feed water solution containing 10 mM of NOM through a NF270 membrane. The low BPA rejection for both 0 and 4 mM of calcium correlates with less fouling compared to 0.5 and 1 mM as described above. This effect may be attributed to limited pore blocking occurring when no calcium is present, thereby resulting in a less dense fouling layer. At a concentration of 4 mM of calcium, large compact aggregates are presumably formed that are too large to block pores and also form a fairly porous cake layer on the membrane surface. An additional effect, the prevention of back diffusion of solute into the bulk solution, has been previ-

ously described (Ng and Elimelech 2004). This results in a higher concentration of the solute at the membrane surface, which eventually leads to a lower rejection. For 0.5 and 1 mM of calcium, respectively, small, coiled macromolecules are formed that can cause pore blocking (Seidel and Elimelech 2002). Besides an increase in fouling, a simultaneous increase in rejection of BPA at these calcium concentrations was observed. Furthermore, the formation of the dense cake layer may induce an additional sieving, which can result in a higher rejection. Both of these mechanisms are thought to occur at the same time and cannot easily be separated.

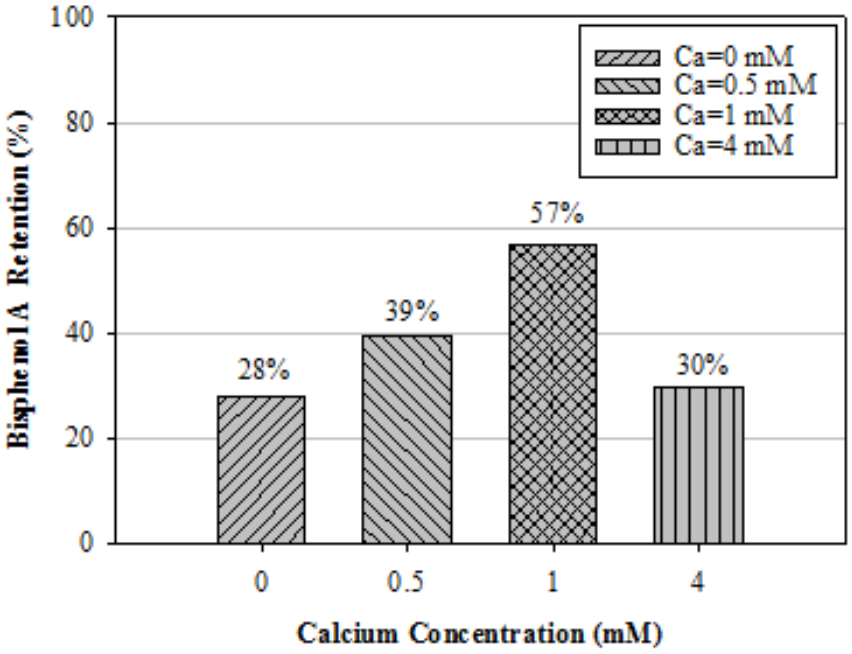


Figure 2-5: Rejection of BPA by NF270 membrane after 420 min (7 h) of membrane rejection test. The feed water contained 750 µg/L of BPA, 1 mM of $NaHCO_3$, 20 mM of NaCl, 20 mg/L of humic acid and variable calcium concentrations, pH = 8.

2.4 Conclusions

The results reported here demonstrate a considerable effect of the feed water calcium concentration on membrane fouling. Fouling was most severe at 0.5 mM, whereas at no calcium or at a higher concentration (e.g. 4 mM) membrane fouling was considerably lower. Two major fouling mechanisms, pore blocking and cake layer formation, are as-

sumed to take place. Both can be caused by solute-solute interactions (bridging and complexation) and solute-membrane interactions (bridging and charge neutralisation). The study also showed a significant influence of fouling on the rejection of BPA. Low rejection coincided with low fouling at 0 mM and 4 mM of calcium, respectively. Rejection increased commensurate with the extent of fouling. However, the highest rejection (at 1 mM of calcium) was not observed when fouling was most severe (at 0.5 mM of calcium). It was hypothesized that pore blocking, which induced an enhanced sieving effect, resulted in an increase in the rejection of BPA. On the other hand, the cake-enhanced concentration polarisation, which hindered back diffusion into the bulk solution, could eventually result in a lower BPA rejection.

3 Characterising humic acid fouling of nanofiltration membranes using bisphenol A as a molecular indicator

3.1 Introduction

Municipal water recycling is an increasingly important strategy for the replacement or augmentation of potable water supplies in many parts of the world. The scope of water recycling schemes is broad, encompassing industrial and agricultural reuse applications, municipal reuse via dedicated recycled water distribution systems and even the direct supplementation of drinking water supplies. Furthermore, the role of membrane filtration in water recycling schemes is steadily growing due to the high water quality that can be achieved at moderate cost (Fane 2007, Verliefde et al. 2007a).

A major benefit of the deployment of membrane filtration technology in water recycling schemes is the removal of micropollutants which are ubiquitously detected in secondary treated effluent at trace concentrations. Despite the importance of membrane filtration processes in the water industry, current knowledge regarding the fundamental mechanisms that lead to the separation of trace organic contaminants remains limited. Recent review articles have highlighted the fact that these removal mechanisms are complex and can be governed by many factors including membrane characteristics, physico-chemical properties of the solutes, and solution chemistry (Bellona et al. 2004, Nghiem and Schäfer 2005). Moreover, understanding of the rejection behaviours of trace organic contaminants under realistic conditions is still quite poor. In particular, very little is known about the effects of membrane fouling, which is inherent in full scale operation, on the rejection of trace organic contaminants (Bacchin et al. 2006, Fane 2007).

Fouling presents one of the most challenging issues to the design and management of membrane filtration systems. It has been defined as 'the process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings or within its pores (Koros et al. 1996). Although membrane fouling can be reduced through appropriate design, operation and cleaning, some degree of fouling is inevitable in full scale applications (Bacchin et al. 2006, Fane 2007). In municipal water recycling applications, fouling by associated organic matter is expected to be the most prevalent form of membrane fouling. Previous studies have demonstrated that organic fouling is most severe under conditions of low pH, high ionic strength, and particularly in the presence of calcium ions (Li and Elimelech 2004, Manttari

et al. 2000, Schäfer et al. 1998, Yuan and Zydney 2000). Furthermore, fouling of NF membranes by organic matter is mainly attributed to pore blocking, which can be classified into three categories: complete pore blocking (blocking of a pore by solutes approximately the same size as the pore), incomplete or intermediate pore blocking, and standard pore blocking (gradual pore narrowing and constriction by adhesive solutes that are much smaller than the pore) (Al-Amoudi and Lovitt 2007). It is noteworthy that most existing studies have investigated organic and colloidal fouling with an emphasis on the impacts on permeate flux and inorganic salt rejection. The effects of membrane fouling on the rejection of trace organic chemicals have been only recently and briefly investigated. However, it has been demonstrated that membrane fouling can significantly influence the separation of trace organic contaminants particularly by NF membranes (Agenson and Urase 2007, Plakas et al. 2006). Xu et al. (2006) showed that membrane fouling caused by secondary treated effluent significantly affected the rejection of trace organics by NF and ultra-low-pressure RO membranes, whereas it was less important for more conventional RO membranes. This observation is consistent with our previous investigation of the influence of organic fouling on the removal of hydrophilic pharmaceuticals by NF membranes (Nghiem and Hawkes 2007). In that study, we demonstrated that membrane pore size played an important role in governing the effects of fouling on the rejection of hydrophilic trace organics. Nonetheless, the impact of membrane fouling on other important rejection mechanisms, such as hydrophobic adsorption and electrostatic repulsion, remains poorly understood.

This study aimed to elucidate the effects of membrane fouling by close examination of the key mechanisms of rejection of bisphenol A by NF processes. BPA is a ubiquitous trace organic contaminant in secondary treated effluent, but was selected primarily because of its suitable physical dimensions and physicochemical properties to provide indicatively variable rejection behaviour under variable conditions. Three commercially available NF membranes with differ-rent average pore sizes were selected for this investigation. Membrane fouling was induced by a foulant mixture containing humic acid as a model organic foulant in a background electrolyte solution. The effects of membrane fouling on the rejection of BPA were observed with respect to the membrane pore sizes and the fouling characteristics. Mechanisms possibly accountable for the effects of membrane fouling on BPA rejection were systematically investigated and proposed.

3.2 Materials and methods

3.2.1 Model NF membranes and membrane characterisation

Three commercially available NF membranes – denoted NF90, NF270, and TFC-SR2 – were used in this investigation. The first two membranes were supplied by Dow FilmTec (Minneapolis, MN, USA) and the third was supplied by Koch Membrane Systems (San Diego, CA, USA). According to the manufacturers, these membranes are polyamide thin-film composite with a microporous polysulfone supporting layer. The nominal operating permeate fluxes are 41, 52, and 50 L m^{-2} h^{-1} at 480, 480, and 380 kPa transmembrane pressure for the NF90, NF270, and TFC-SR2 membranes, respectively. These membranes were received as flat sheet samples and were stored dry at 4 °C. All membrane samples were rinsed thoroughly with Milli-Q water prior to use. The membrane average pore diameters were estimated in a previous study by challenging the membranes with a series of low molecular weight carbohydrate compounds under various permeate flux conditions and applying a pore transport model (Nghiem et al. 2004).

Contact angle measurement of the clean and fouled membranes was performed with a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ, USA) using the standard sessile drop method. Milli-Q water was used as the reference liquid. The fouled membranes were air dried prior to the measurement. At least five droplets were applied onto duplicate membrane samples and contact angle was measured on both sides of the droplet.

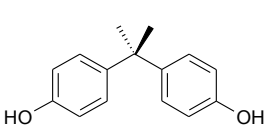
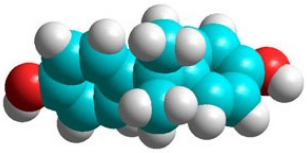
Surface morphology of the membrane was analysed using a multimode atomic force microscope (AFM) (Digital Instruments, Santa Barbara, CA, USA). Imaging was undertaken in air in tapping mode operation using an oxide sharpened SiN probe. The membrane average surface roughness was determined in triplicate by AFM image analysis over a 2 µm x 2 µm surface area.

3.2.2 Model trace organic contaminant

BPA is a common micropollutant, often reported at trace levels in sewage and secondary effluent (see for example, Lee and Peart (2000) and Fromme et al. (2002)). Higher concentrations of this compound, up to several milligrams per liter, in landfill leachate have also been reported (Yamamoto et al. 2001). Molecular dimensions and key physicochemical properties of this compound are shown in Table 3-1. The molecular length was defined as

the distance between the two most distant atoms in the molecule and molecular width and height were dimensions perpendicular to the molecule longitudinal axis. These values were computed using the ChemOffice program based on the most stable configuration of the molecule. The dimensions of BPA are comparable to the pore size range of nanofiltration membranes, thus allowing a more systematic investigation of the physico-chemical interactions underlying the effects of membrane fouling on the rejection of small organic solutes. BPA has a moderately high octanol-water partitioning coefficient (log K_{OW}), which indicates possible adsorption of this compound to hydrophobic materials such as membrane surfaces. BPA is a weak acid having a pK_a of 10.1. Accordingly, at environmental pH ranges, the compound is not significantly dissociated and it exists predominantly as a neutral species. A stock solution containing 1 g/L of BPA (Sigma-Aldrich, Castle Hill, NSW, Australia) was prepared in pure methanol (HPLC grade). The stock solution was stored in a freezer at -18°°C and used within 1 month of preparation.

Table 3-1: Physicochemical properties of Bisphenol A

Formula	$C_{15}H_{16}O_2$	Chemical Structure
Molecular weight (g/mol)	228	 
Molecular width[a] (nm)	0.383	
Molecular height[a] (nm)	0.587	
Molecular length[a] (nm)	1.068	
Solubility in Water (mg/L)	129	
pK_a	10.1	
log K_{ow}	3.32	

[a] Calculated using ChemOffice 2005

3.2.3 Organic foulant

Sigma-Aldrich humic acid (St. Louis, MO, USA) was selected as a model organic foulant in this study. This widely studied humic acid has been thoroughly characterised and previously used in numerous membrane fouling investigations (Manttari et al. 2000, Schäfer et al. 2006, Tang et al. 2007, Yuan and Zydney 1999, Yuan and Zydney 2000). Humic materials are ubiquitous in the aquatic environment. They arise from decay of plant and animal residues such as lignin, protein and carbohydrate that are often found in soil and natural

waters. As a result, humic acid is a complex and heterogeneous association of many macromolecules, which can be described as a supramolecular colloidal mixture (Costa et al. 2006). Carboxylic and phenolic acidity, aromaticity, and molecular weight together with an estimated elementary composition of the selected humic acid are presented in Table 3-2. Possessing several key functional groups including the aliphatic, aromatic, carboxylic and phenolic groups, physicochemical properties of humic acid are expected to vary greatly depending upon the solution chemistry. Ionisation of carboxylic and phenolic groups of humic acid results in electrostatic charges which can induce both inter- and intra-molecular interactions. By modulating these interactions, solution chemistry such as pH and ionic composition can significantly influence the conformational structures of humic acid molecules. Furthermore, it is known that humic acid can act as a complexing agent with multivalent cations such as calcium (Hong and Elimelech 1997, Kilduff et al. 2004, Yoon et al. 1998). The complex interaction amongst humic acid, calcium and functional groups of the membrane surface is thought to be a major factor governing the fouling behaviour of NF membranes. While the carboxylic and phenolic functional groups render humic acid quite hydrophilic, it is also possible for humic acid to exhibit some hydrophobic properties due to the presence of aromatic rings and non-polar aliphatic carbon chains.

Table 3-2: Characteristics of Aldrich humic acid

Elementary Composition [a]						Aromaticity [a]	Phenolic acidity	Carboxylic acidity	Average Molecular weight (g/mol)	
C	H	N	S	O	Ash	(%)	(meq/g)	(meq/g)	M_w	M_n
50.7	4.5	1.2	0.2	31.4	7.5	57.7	3.6 [a]	7.9 [a]	4,006 [a]	1,395 [a]
							1.3 [b]	3.7 [b]	4,100 [c]	1,630 [c]

[a] Ref. (Karanfil et al. 1996)
[b] Ref. (Vermeer and Koopal 1998)
[c] Ref. (Chin et al. 1994)
M_w: Weight – average molecular weight
M_n: Number – average molecular weight

3.2.4 Membrane filtration set-up

A laboratory-scale cross-flow NF/RO membrane rig was used in this study (Figure 3-1). This set-up consisted of a stainless steel plate-and-frame membrane cell with an effective surface area of 23.1 cm^2 (7.7 cm x°3.0 cm), a stainless steel feed reservoir, and a Hydra-

Cell pump (Wanner Engineering Inc., Minneapolis, MN, USA). The permeate flux was monitored by a digital flow meter (Optiflow 1000, J&W Humonics, Folsom, CA, USA) connected to a personal computer. Retentate flow rate was monitored by a rotameter. Feed pressure and cross-flow velocity were controlled by means of a bypass valve and a back pressure regulator. The temperature of the test solution was kept constant using a chiller/heater (Neslab RTE 7, Newington, NH, USA) equipped with a stainless steel heat exchanger coil, which was submerged directly into the feed reservoir.

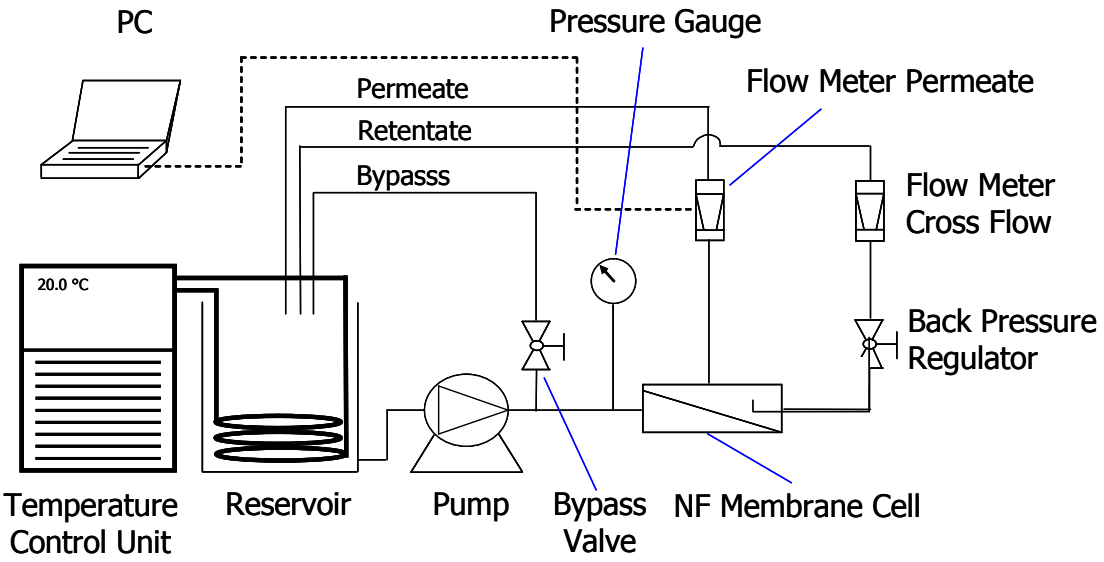


Figure 3-1: Schematic diagram of the laboratory-scale cross-flow nanofiltration test unit

3.2.5 Filtration protocol

The fouling and subsequent rejection experimental protocol was conducted in three steps: membrane pre-compacting, fouling development, and rejection testing. Prior to each membrane filtration test, the membrane was pre-compacted at 1800 kPa for 1 h using Milli-Q water. A fouling layer was then allowed to develop using a foulant mixture comprising a specific amount of humic acid in an electrolyte matrix containing 20 mM NaCl, 1 mM $NaHCO_3$, and a varying amount of $CaCl_2$. The volume of the feed water solution used in each experiment was 7 L. Following the addition of the foulants, the cross-flow velocity and permeate flux were adjusted to be 30.4 cm s^{-1} and 48.5 µm s^{-1} (175 L m^{-2} h^{-1}), respectively. This initial permeate flux was defined as J_0. The fouling development step was carried out under a constant pressure until a stable permeate flux had been observed which usually took approximately 18 h. Throughout the experiment, both the

retentate and permeate were recycled back to the feed reservoir. After the fouling development, the permeate flow rate was set to 15 μm s^{-1} (54 L m^{-2} h^{-1}). This was comparable to the permeate fluxes recommended by the manufacturers (see Section 3.2.1). Following permeate flux adjustment, BPA was spiked into the feed solution to make up a concentration of 750 mg/L. Samples of feed and permeate (ca. 1.5 mL) were collected at specified intervals for analysis. Throughout the filtration experiments, the temperature of the solution was maintained at 20 ± 0.1° C. To examine BPA rejection by the clean (non-fouled) membranes, a similar protocol was adopted, but without the fouling development step. Observed contaminant rejection is defined as $R = 100 \times (1 - C_P/C_F)$, where C_P and C_F are the permeate and the feed concentrations, respectively.

3.2.6 Analytical technique

A Shimadzu HPLC system (Kyoto, Japan) equipped with a Discovery® C18 column (with diameter, length and pore size of 4.6 mm, 150 mm and 5 μm, respectively) was used for the analysis of BPA. Detection was undertaken by ultraviolet (UV) absorption at 280 nm. Premixed mobile phase was prepared using HPLC grade acetonitrile (ACN) and an aqueous KH_2PO_4 (25 mmol/L) buffer solution. Two mobile phase solutions were prepared and designated as Eluent A (80% ACN/20% buffer solution) and Eluent B (20% ACN/80% buffer solution). The flow rate was 1 mL/min and a sample injection volume of 50 mL was used. Calibration standards were prepared in Milli-Q water. In the range of experimental concentrations used, a linear calibration curve was obtained with coefficient of determination (R^2) of 0.99. The analysis was carried out immediately on the conclusion of each experiment.

Non-purgeable TOC was measured with a Shimadzu TOC V-CSH analyzer (Kyoto, Japan). TOC samples were collected prior to the addition of BPA. Sodium and calcium were analysed using a Varian Atomic Adsorption Spectrophotometer.

3.3 Results and discussions

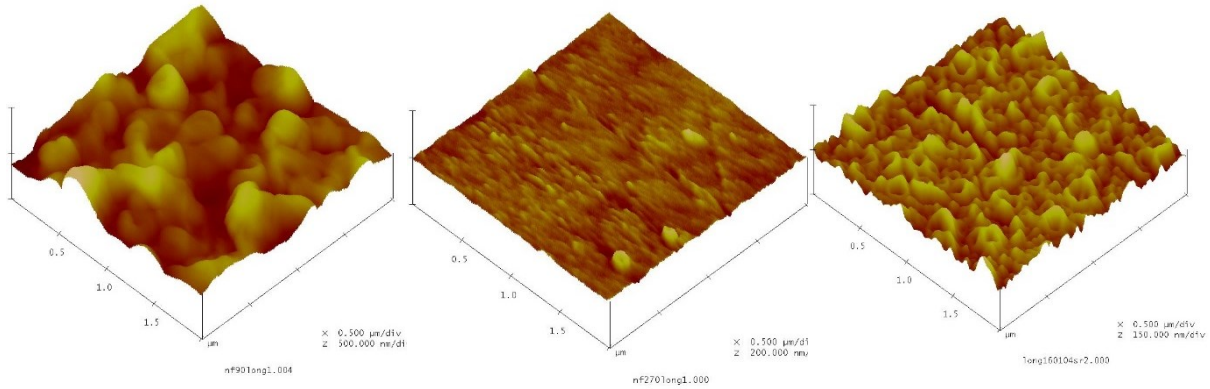
3.3.1 Membrane characteristics

The nanofiltration membranes selected for this study are each comprised of a very thin active layer on top of a porous polysulfone backing layer. The active layer of the NF270

membrane is made of semi-aromatic piperazine-based polyamide, while both the NF90 and TFC-SR2 membranes have a fully aromatic polyamide active layer. These three membranes have quite distinctive characteristics as shown in Table 3-3. They represent a wide range of membrane pore size, with pore size increasing in the order: NF90 < NF270 < TFC-SR2. The NF90 is a relatively tight NF membrane with an average pore diameter of only 0.68 nm. In contrast, the NF270 can be considered as a loose NF membrane (0.84 nm) and the TFC-SR2 is a very loose NF membrane (1.28 nm). The pore sizes of the two looser membranes are comparatively larger than the dimensions of the BPA molecule (Table 3-1). The membrane pore sizes were well correlated with their sodium and calcium chloride rejection (Table 3-3). It is noteworthy that both sodium and calcium chloride rejections of the TFC-SR2 were very low and this membrane can in fact be considered as a UF membrane based on the definition of inorganic salt rejection. Despite their significant differences in porosity, all three membranes showed a good humic acid removal capacity. High humic acid rejection (measured by TOC) could be attributed to the high average molecular weight of this organic foulant (see Table 3-2). Surface topography analysis by the AFM undertaken in tapping mode reveals that both the NF270 and TFC-SR2 have a very smooth surface with mean roughness of only 8.55 nm and 8.13 nm, respectively. In contrast, surface roughness of the NF90 is quite high and comparable to those of typical RO membranes (in the range of tens of nanometres) (Freger et al. 2002). AFM images of the three NF membranes are shown in Figure 3-2. Contact angle measurement indicates that the NF90 membrane is moderately hydrophilic (contact angle of 42.2°), whereas the NF270 and TFC-SR2 membranes are very hydrophilic with contact angles of only 23.4° and 18.7°, respectively. The resistance of the NF270 membrane to organic fouling has previously been attributed to its hydrophilic nature (Mänttäri et al. 2004).

Table 3-3: Properties of the membranes used in this study

Membrane	Pure water permeability ($Lm^{-2}h^{-1}bar^{-1}$)	Average pore diameter (nm)	Roughness (nm)	Contact angle (^{O})	NaCl rejection (%)	$CaCl_2$ rejection (%)	TOC rejection (%)
NF90	6.4	0.68	76.8	42.2	85.0	95.0	92.7
NF270	13.5	0.84	8.55	23.4	40.0	43.0	88.9
TFC-SR2	15.4	1.28	8.13	18.7	9.8	21.2	82.8



NF90 membrane NF270 membrane TFC-SR2 membrane

Figure 3-2: Surface topography of the NF90, NF270, and TFC-SR2 membranes.

3.3.2 Membrane fouling behaviour

Humic acid and calcium in the membrane feed were clearly observed to be significant factors in the determination of permeate flux. Figure 3-3 shows the normalised permeate flux over time during the fouling layer development phase with variable feed compositions for 18 h. While membrane fouling was not observed in the absence of humic acid, fouling was quite severe with feed solutions containing 20 mg/L humic acid. Furthermore, the extent of fouling was dependent on the calcium concentration in the feed solution. The role of multivalent cations such as calcium in organic fouling has been discussed in conjunction with several previous studies (Hong and Elimelech 1997, Seidel and Elimelech 2002). It has been suggested that calcium plays a major role in intermolecular bridging between organic foulants and the membrane surface (Seidel and Elimelech 2002). Furthermore, calcium could form complexes with polar functional groups of the humic acid (solute-solute interactions), resulting in a reduction in electrostatic repulsion between the functional groups, thus leading to the formation of small and coiled macromolecules. Calcium might also neutralise the negative charge of both the membrane surface and the humic acid molecules causing a decrease in their electrostatic interaction (Yoon et al. 1998).

Two distinct fouling stages were observed with all three membranes, possibly associated with two different fouling mechanisms. The flux decreased sharply during the first 8 h of each filtration experiment. This initial rapid fouling stage was interpreted as being caused

by adsorption of humic acid to the membrane surface and pore blocking. This is consistent with previous discussion that pore blocking due to the small flocs was a major reason for the most severe fouling when 0.5 mM or 1 mM of calcium was present in the feed solution (Nghiem et al. 2006b). In contrast, after the initial rapid fouling stage, the rate of flux decline became more gradual. Furthermore, the flux decline profiles appeared to cease to be dependent on calcium concentration during the later stages (Figure 3-3). On the other hand, compaction and thickening of the cake layer could be attributed to the second fouling stage.

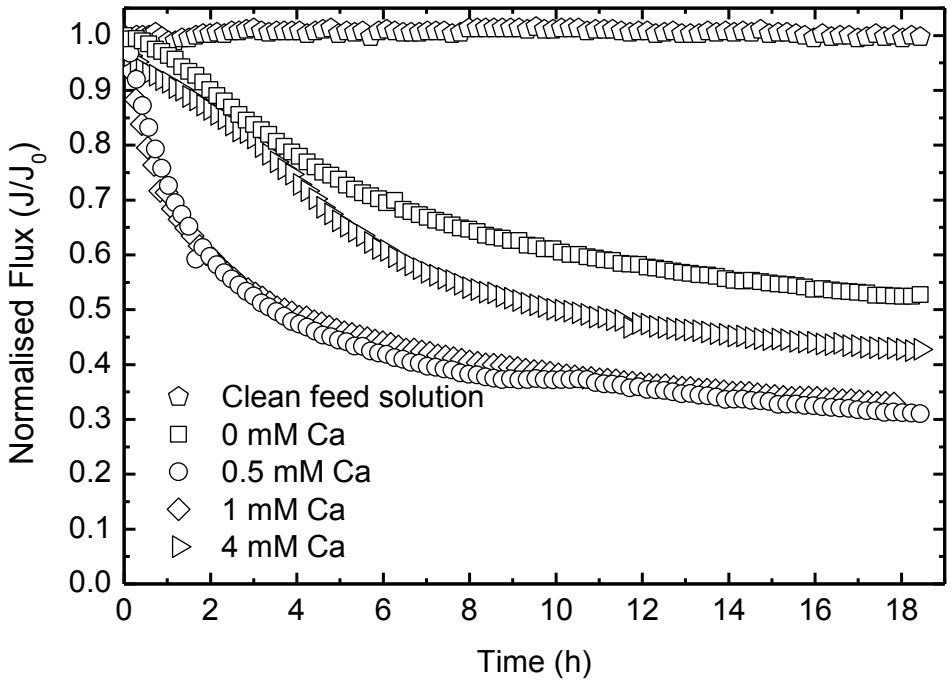


Figure 3-3: Influence of calcium concentration in the feed solution on permeate flux of the NF270 membrane. The feed water contained 1 mM of $NaHCO_3$, 20 mM of NaCl, 20 mg/L of humic acid (no humic acid for clean water test) and variable calcium concentrations, pH = 8.

Figure 3-4 shows the normalised flux of the three membranes during fouling development under the same experimental conditions and with the same initial permeate flux. Despite being the smoothest and most hydrophilic membrane (Table 3-3), the TFC-SR2

exhibited the most severe fouling. This could possibly be attributed to pore blocking and the fact that the TFC-SR2 has a relatively large average membrane pore size. It is noteworthy that the equivalent Stokes radius of humic acid molecules calculated based on the Wilke-Chang and Stokes-Einstein equations (Geankoplis 1993) from their number-average molecular weight as shown in Table 3-2 were in the range of 0.947 - 1.02 nm and thus pore plugging of the TFC-SR2 membrane is plausible.

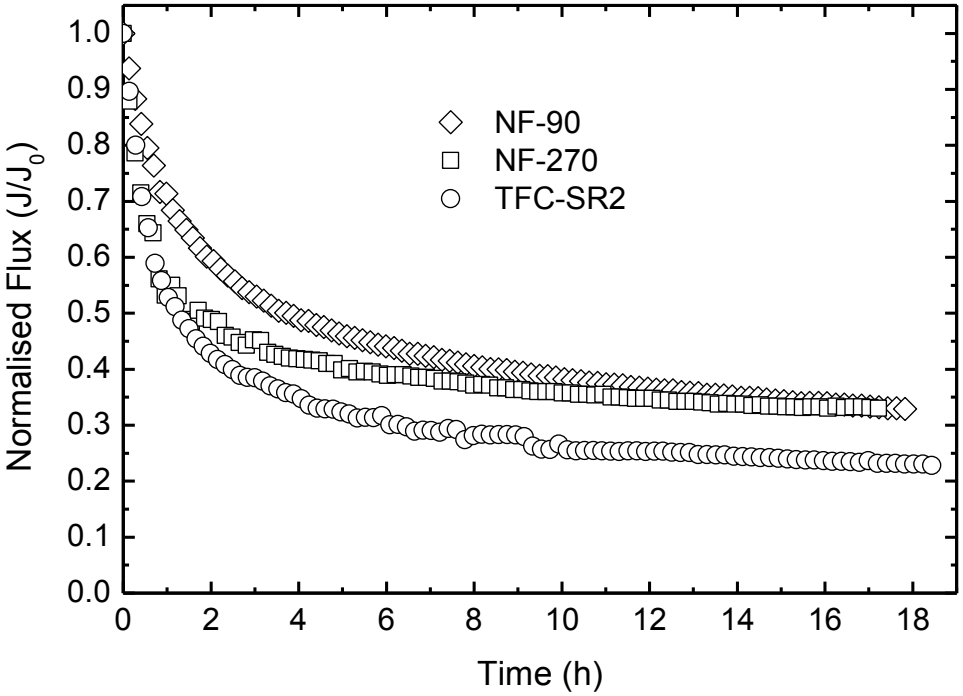


Figure 3-4: Normalised permeate flux of the three membranes - NF90, NF270, and TFC-SR2 - as a function of filtration time. (Feed solution: 1 mM of $NaHCO_3$, 20 mM of NaCl, 1 mM of $CaCl_2$, and 20 mg/L of humic acid).

Interestingly, there appears to be a critical concentration of calcium, at which fouling was most severe (Figure 3-5). The relative extent of flux decline after 18 h for the NF270 membrane was as follows: 0.5 mM > 1 mM > 4 mM > 0 mM. This was consistent with a previous study, which showed a peak in membrane fouling in the ultrafiltration of greywater at a similar calcium concentration (Nghiem et al. 2006b). It is noteworthy that as the calcium concentration of the foulant mixture increased beyond this apparent critical concentration of approximately 0.5 - 1 mM of Ca^{2+}, a reduction in the rate of membrane fouling could be observed. This is also consistent with the results obtained with the NF90 and the

TFC-SR2 membranes. For both of these membranes, the most severe fouling condition was obtained with a feed solution containing 1 mM of Ca^{2+} in the presence of 20 mg/L humic acid (see Figure 3-5). It was hypothesised that a high calcium concentration might lead to the formation of large and compact aggregates (or flocs) and that these may result in a more porous cake layer. Furthermore, it was also probable that these aggregates could not penetrate into the membrane leading to pore blocking. In contrast, at lower calcium concentrations aggregates formed were smaller which is consistent with previous observations for colloidal systems (Waite 1999).

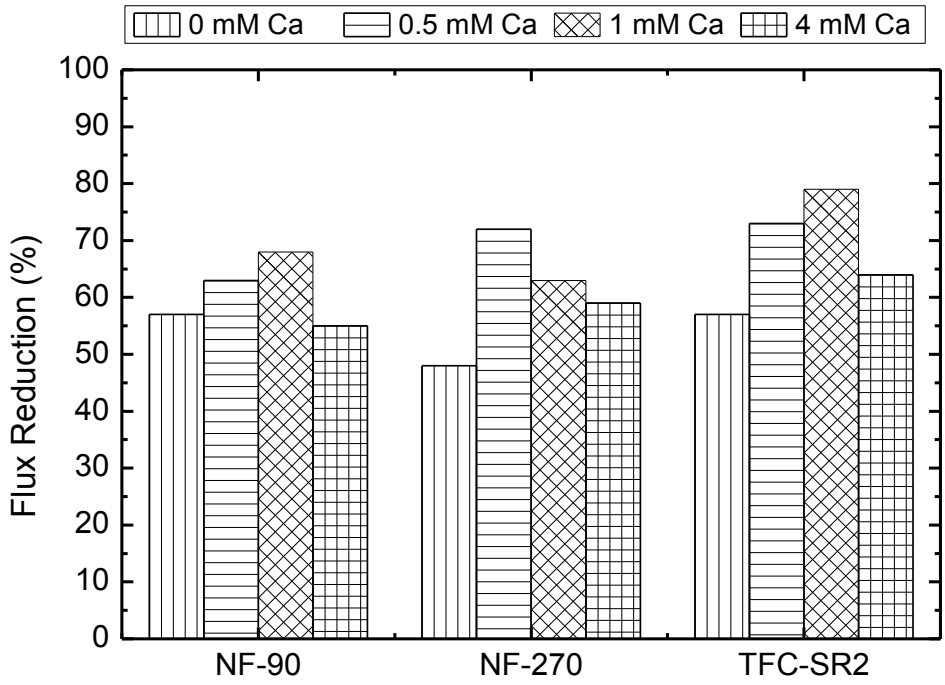


Figure 3-5: Reduction in permeate flux after 18 h fouling development as a function of Ca^{2+} in the feed solution (Flux reduction is defined as 100 x ($1-J_{18\,h}/J_0$). Feed solution contained 1 mM of $NaHCO_3$, 20 mM of NaCl, 20 mg/L of humic acid, and variable $CaCl_2$ concentrations, pH = 8.

3.3.3 Change of membrane hydrophobicity

A dark brown layer of humic foulant firmly attached to the membrane surface was observed subsequent to all fouling experiments. As discussed previously, due to the aromatic and aliphatic components of humic acid and the possibility that calcium may chelate

with the carboxylic and phenolic groups, hence reducing electric charge of the humic acid solution molecules, the organic fouling layer would be expected to be quite hydrophobic. This hydrophobicity was clearly observed by a considerable increase in contact angle of all three membranes fouled with humic acid compared to their clean (unfouled) condition (Figure 3-6). The similarity in contact angles of the fouled membranes indicates that membrane hydrophobicity is primarily governed by the adhesion of the humic acid layer irrespective of the initial clean membrane surface characteristic. Results shown in Figure 3-6 also suggest that the humic acid foulant layer can compete with the membrane for hydrophobic interaction with hydrophobic compounds such as BPA. Consequently, this hydrophobic fouling layer can potentially influence the separation of BPA by the NF filtration processes.

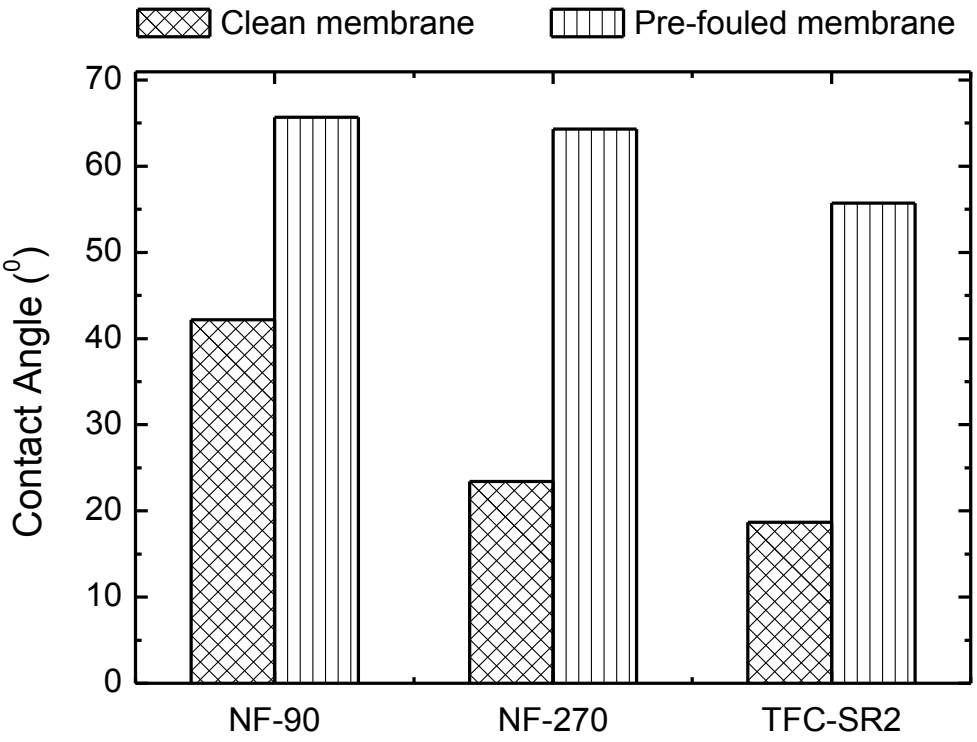


Figure 3-6: Change in membrane surface hydrophobicity due to humic acid fouling of the NF90, NF270 and TFC-SR2 membranes. Fouling was developed with a feed solution containing 1 mM of $NaHCO_3$, 20 mM of NaCl, 1 mM of $CaCl_2$, and 20 mg/L of humic acid, pH = 8.

3.3.4 Effects of organic fouling on the nanofiltration of BPA

To examine the effect of organic fouling on the rejection of trace organics, BPA was spiked into the feed solution after a fouling layer on the membrane surface had been established. Mass balance analysis indicated considerable adsorption of BPA to the membrane in all experiments. Such adsorption was evident by a sharp increase in BPA concentration in the permeate before reaching a stable value as can be seen in Figure 3-7, which shows BPA concentrations in the feed and permeate over time for two typical experiments by the NF270 membrane. The NF270 is a relatively loose nanofiltration membrane with pore size slightly larger than the molecular width and height of BPA. Consequently, initial low concentration of BPA in the permeate can be attributed to the adsorption of this compound to the membrane. Due to the small membrane sample size in comparison to the amount of BPA used in this study, the decrease in BPA concentration in the feed solution was small, but nevertheless apparent (Figure 3-7). It is noted that no discernible adsorption of BPA to the test equipment or degradation of BPA could be observed and the concentration of BPA remained constant after a BPA solution was circulated within the filtration system without a membrane sample for 10 h. Previous studies have suggested that adsorption of trace organics to the membrane polymer could result in a lower rejection due to diffusional transport of the solute across the active layer of the membranes (Nghiem et al. 2004, Nghiem et al. 2005b, Zhang et al. 2006).

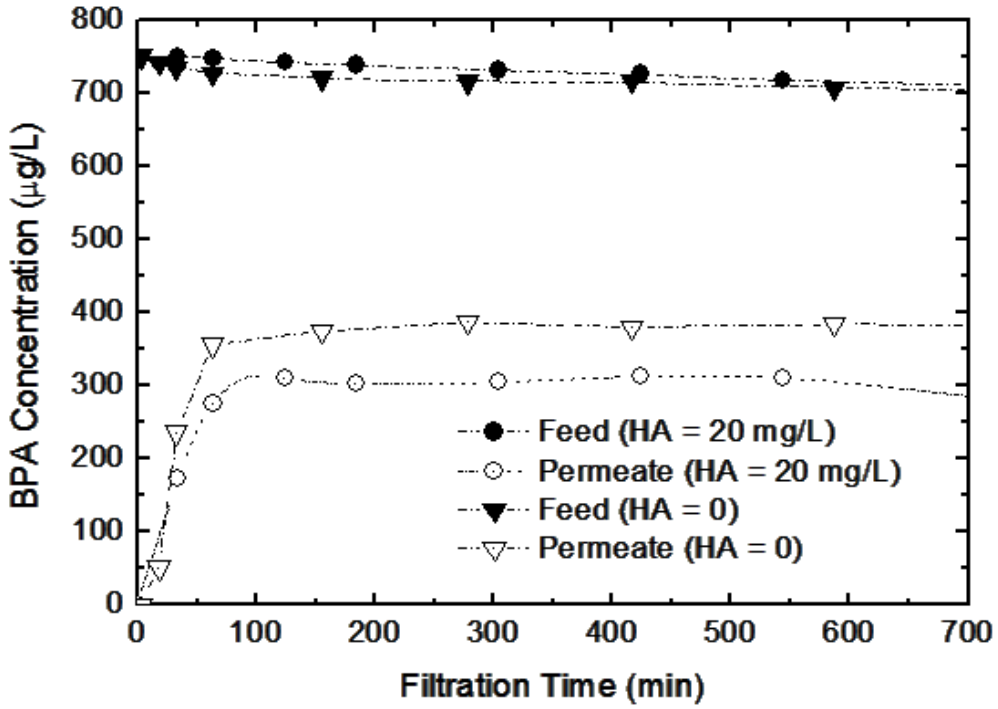


Figure 3-7: Concentrations of BPA in feed water and permeate and rejection of BPA by the NF270 membrane under clean and fouled conditions. The feed water contained 750 μg/L of BPA, 1 mM of $NaHCO_3$, 20 mM of NaCl, 1 mM of $CaCl_2$, and 0 or 20 mg/L of humic acid, pH = 8.

While adsorption of BPA to the membrane occurred to the same extent under both clean and fouled conditions based on a mass balance calculation, an interesting observation was that the stabilised BPA concentration in the permeate varied considerably depending on the extent of membrane fouling. Results reported in Figure 3-7 are consistent with a study of Xu et al. (2006), who also reported an increase in rejection (or decrease in permeate concentration) of hydrophobic trace organics by fouled membranes. It is possible that the formation of a hydrophobic membrane fouling layer could isolate and thus hinder the interactions between the membrane and the solutes. This could result in less solute partitioning and diffusion across the membrane, which has been reported as a major transport mechanism of hydrophobic solutes in NF and RO filtration processes (Bellona et al. 2004, Nghiem et al. 2004). The overall effect of membrane fouling on the rejection of BPA is, however, quite complex and can be attributed to several antagonistic mechanisms, which will be discussed in detail in the next section.

3.3.5 Effects of organic fouling on rejection: the mechanisms

It is hypothesised that the presence of a fouling cake layer could lead to a phenomenon known as cake-enhanced concentration polarisation as previously reported by Ng and Elimelech (2004). The cake layer hindered the diffusion of BPA back to the bulk solution resulting in an elevated concentration of BPA within the cake layer. Consequently, this led to an increased concentration gradient of BPA across the membrane, and hence, a lower rejection. This phenomenon resulted in a considerably lower BPA rejection by the NF270 membrane previously fouled using foulant mixtures containing 0 and 4 mM of Ca^{2+} as compared to the rejection under an unfouled or clean membrane condition (represented by a dotted line in Figure 3-8). It is noteworthy that experiments under unfouled membrane conditions were conducted in duplicate and the deviation between two repeated experiments was less than 5%.

In contrast to the deleterious effect of cake-enhanced concentration polarisation on BPA rejection, membrane fouling caused by pore blocking could considerably enhance solute rejection. As discussed above, pore blocking could occur at a critical calcium concentration in the feed (0.5 - 1 mM of Ca^{2+}). Indeed, BPA rejection was observed to be significantly increased under such conditions (Figure 3-8). Most notably, when the foulant mixture contained 1 mM of Ca^{2+}, BPA rejection increased even above that observed during clean membrane experiments. This effect on BPA rejection, presumed to be caused by pore blocking, was much more obvious for the comparatively very loose TFC-SR2 membrane. As can be seen in Figure 3-8, BPA rejection by the TFC-SR2 was significantly enhanced under fouled conditions. Moreover, the magnitude of such enhancement was well correlated to the extent of membrane fouling (Figure 3-9). An increase of almost 30% in rejection was observed under the most severe fouling condition. It is noted that the cake-enhanced concentration polarisation effect could be minimal for the TFC-SR2 membrane as this membrane would cause negligible concentration polarisation due to its relatively large pore size.

A small but nevertheless apparent increase in BPA rejection by the NF90 membrane under fouled conditions can also be observed in Figure 3-8. The NF90 membrane has an average pore diameter of only 0.68 nm, which is in the same order or smaller than the dimensions of the BPA molecule. Therefore, this increase in BPA rejection could only be attributed to pore blocking to a limited extent. More importantly, as previously discussed the presence of a fouling layer on the membrane surface could separate and therefore interfere with the interaction between the BPA molecule and the membrane surface.

While mass balance analysis revealed that BPA losses (presumably due to adsorption) under both clean and fouled conditions were similar, it appears probable that under fouled conditions, a substantial proportion of BPA has adsorbed to the fouling layer which was quite hydrophobic (see Figure 3-6). Consequently, this could hinder BPA from partitioning and diffusing across the polymeric membrane, resulting in a small increase in rejection under fouled conditions.

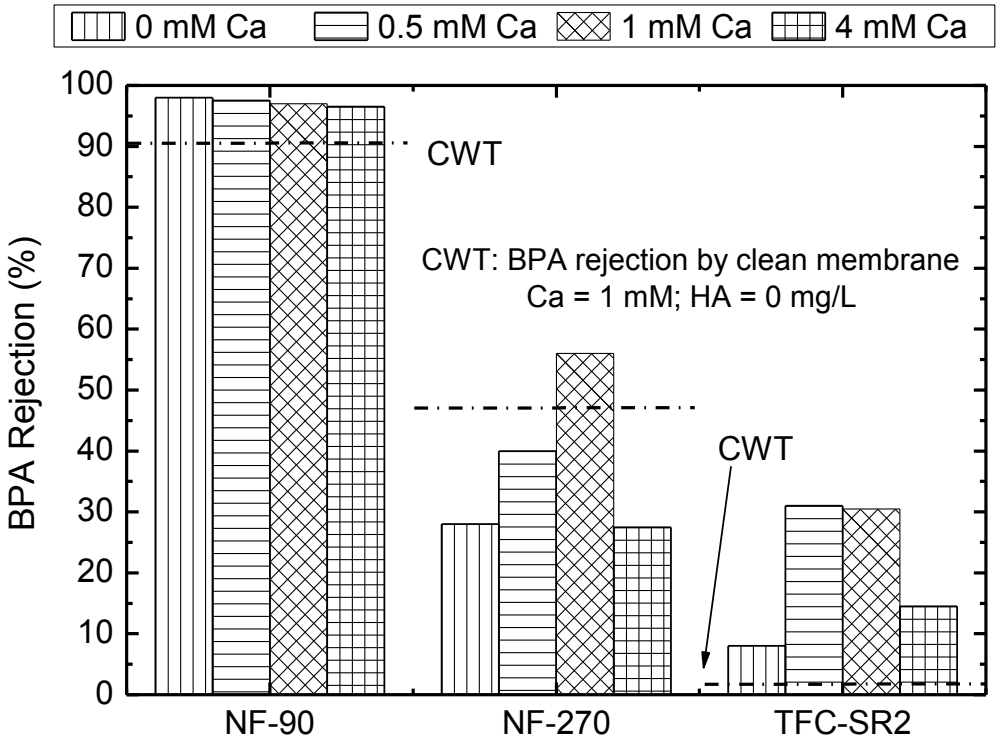


Figure 3-8: Rejection of BPA by the NF90, NF270 and TFC-SR2 membranes under various fouling condition (value taken after stabilising the system for 10 hours to avoid any adsorption artifact). Broken line shows BPA rejection under clean condition by the three membranes. The feed water contained 750 µg/L BPA, 1 mM $NaHCO_3$, 20 mM NaCl, 20 mg/L humic acid and variable $CaCl_2$ concentrations, pH = 8.

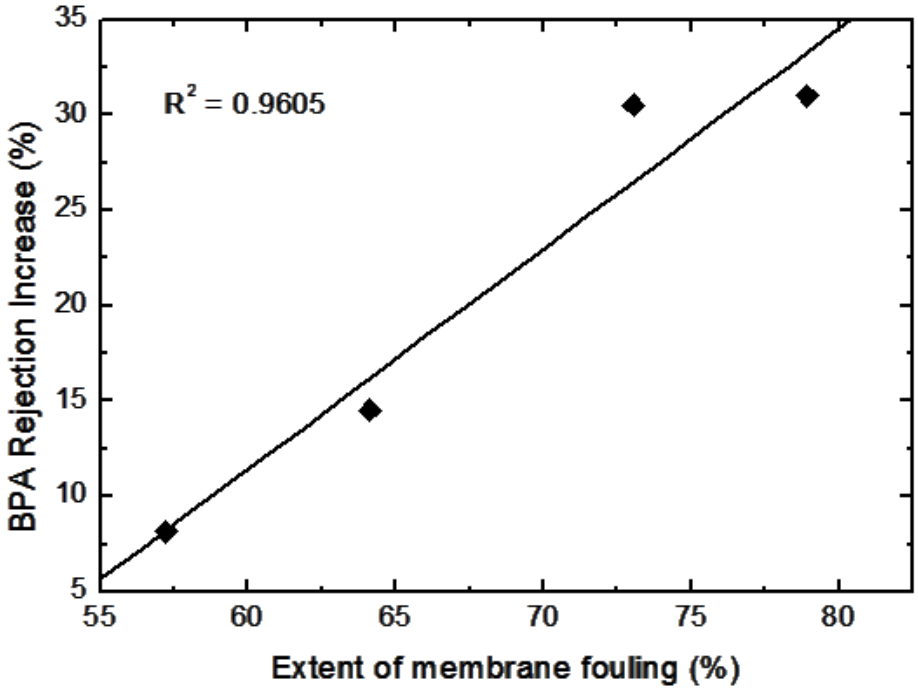


Figure 3-9: Correlation between the extent of membrane fouling (presented by flux reduction) and increase in BPA rejection by the TFC-SR2 membrane. Experimental conditions are as in the captions of Figures 3.5 and 3.8.

3.4 Conclusions

Results reported here indicate that calcium concentration in the feed solution could be a significant factor governing humic acid fouling processes. Moreover, there appears to be a critical concentration of calcium in the feed solution, at which membrane fouling is most severe. Membrane fouling was found to have a considerable influence on the separation process of the model trace contaminant BPA. Such influence resulted in either an increase or decrease in rejection and this was interpreted as being a function of competing fouling mechanisms. These mechanisms could occur simultaneously and their individual effects may not be easily distinguished. However, their relative contribution appears to be membrane pore size dependent. Pore blocking, which resulted in a considerable improvement in rejection, was prominent for the larger pore size TFC-SR2 membrane. In contrast, the cake-enhanced concentration polarisation effect appeared to be more significant for the

tighter NF270 and NF90 membranes. The formation of the fouling layer could also interfere with the solute-membrane interaction, particularly when both the solute and foulant layer are hydrophobic, and therefore, exert a considerable influence on the separation process.

4 Effects of fouling and scaling on the rejection of trace organic contaminants by a nanofiltration membrane: The role of cake-enhanced concentration polarisation

4.1 Introduction

The widespread occurrence of trace organic contaminants in various matrices of the natural environment has recently been reported in the literature (Kolpin et al. 2002, Kümmerer 2009, Ternes 1998). Most of these contaminants originate from anthropogenic sources such as personal care products, human and veterinary pharmaceuticals, industrial chemicals, and agrochemical products. Various adverse effects including those on the reproductive and endocrine systems particularly of aquatic species have been reported (Kümmerer 2009, Milnes et al. 2006). Sewer systems are considered a major pathway for trace organic contaminants into the aquatic environment since these compounds are not completely removed by conventional wastewater treatment. This leads to the widespread occurrence of trace organic contaminants in wastewater effluent impacted freshwater bodies, where they have been detected at levels ranging from a few ng/L up to several µg/L (Kolpin et al. 2002, Ternes 1998). This is of particular importance for applications of direct or indirect potable reuse of reclaimed water, which have become very popular around the world due to an increasing scarcity of suitable freshwater sources.

Nanofiltration and reverse osmosis have been recognised as attractive technologies for producing high quality water from non-traditional sources such as brackish or sea water and secondary treated effluent. Previous studies have conclusively demonstrated the excellent capability of NF/RO to retain a wide range of trace organic contaminants (Agenson and Urase 2007, Bellona and Drewes 2007, Radjenovic et al. 2008, Verliefde et al. 2007a, Verliefde et al. 2009, Yangali-Quintanilla et al. 2009, Yoon and Lueptow 2005, Yoon et al. 2007). These studies also revealed the complexity of the separation process involved. In addition, various parameters such as membrane properties, solution chemistry, and physicochemical properties of the trace organic contaminants can substantially alter the removal efficiency of these solutes by NF/RO membranes (Bellona et al. 2004, Nghiem et al. 2004, Nghiem et al. 2006b, Verliefde et al. 2008). Indeed, studies reported to date demonstrated a great variability in the actual rejection values of the individual trace organic contaminants. In particular, a recent pilot scale study has shown that membrane fouling can also affect the rejection of trace organic contaminants by NF/RO membranes (Xu et al. 2006a).

Fouling and, to a lesser extent, scaling are problematic and inherent to almost all membrane filtration processes (Li and Elimelech 2006, Schäfer et al. 2005). Membrane fouling occurs as common impurities of the feed solution such as dissolved organics and colloidal matter are deposited on the membrane surface to form a cake layer (Schäfer et al. 2005). Biofouling can also occur due to the colonisation of bacteria on the membrane surface (Schäfer et al. 2005). The precipitation of sparingly soluble salts on the membrane surface (or membrane scaling) is another serious issue in NF/RO membrane applications (Sheikholeslami 2004, Tzotzi et al. 2007). Membrane scaling can lead to not only a severe decline in permeate flux but also a considerably shortened membrane lifetime. While the issue of membrane fouling and scaling has been a subject of many dedicated studies, the majority of these studies have focused exclusively on permeate flux decline. Investigations delineating the influence of membrane fouling and scaling on the rejection of trace organic contaminants remain limited. In addition, studies available to date have looked mostly at the effect of a single fouling layer on the rejection of trace organic contaminants using a single type of foulant such as organics or silica colloids to simulate membrane fouling (Nghiem et al. 2010, Nghiem et al. 2008, Nghiem and Hawkes 2007, 2009, Verliefde et al. 2009, Yangali-Quintanilla et al. 2009). This simplified experimental approach enables the systematic elucidation of key mechanisms governing the influence of membrane fouling on the rejection of trace organic contaminants by NF/RO membranes (Nghiem et al. 2010). However, membrane fouling caused by a single type of foulant is rare in a practical application. As a consequence, some researchers have recently started to examine the simultaneous fouling process caused by several different foulants (Contreras et al. 2009, Jarusutthirak et al. 2007, Lee et al. 2005, Li and Elimelech 2006). Not surprisingly, fouling behaviour caused by multiple foulants can substantially differ from that caused by a single foulant. For example, Li and Elimelech showed that membrane fouling developed at a significantly higher rate in combined fouling experiments than might have been predicted by summing up the contributions from each individual foulant as determined in single foulant fouling tests (Li and Elimelech 2006). The authors attributed the observed synergistic fouling to the hindrance of back diffusion of each foulant (Li and Elimelech 2006).

Despite the fact that membrane scaling can occur quite frequently in water recycling applications using NF/RO technologies, effects of membrane scaling on the rejection of trace organic contaminants remain poorly understood. In such applications, interactions between organic matter and scale forming inorganic salts can be quite complex. For example, Lee et al. reported that humic acids can act as an anti-scalant and substantially influence both the morphology and the formation rate of $CaSO_4$ scaling (Lee et al. 2009).

In a number of other studies, the ability of natural organic matter to interfere with the formation of $CaCO_3$ precipitates has also been demonstrated (Amjad et al. 1998, Klepetsanis et al. 2000, Zuddas et al. 2003).

This paper aims to investigate the combined impact of organic fouling and inorganic scaling on the rejection of three selected trace organic contaminants - sulfamethoxazole, bisphenol A, and carbamazepine - by a commercially available nanofiltration membrane. Organic fouling and inorganic scaling were induced sequentially using humic acid and $CaCO_3$. The selected membrane as well as the fouling and scaling processes were characterised in detail. The effect of membrane fouling/scaling on the rejection of the trace organic contaminants were discussed and related to the morphology of the scaling layer. Mechanisms possibly responsible for the effects of membrane fouling/scaling on the rejection of trace organic contaminants were proposed and delineated.

4.2 Materials and methods

4.2.1 Nanofiltration membrane

Flat sheet samples of a thin film composite NF membrane - NF270 (Dow FilmTec, Minneapolis, MN, USA) - were used in this investigation. According to the manufacturer, the nominal permeate flux of this membrane is 52 L m^{-2} h^{-1} and the maximum pressure tolerance is 41 bar. The pH range for continuous operation of this membrane is 2 - 11. The membrane was received as flat sheet samples and was stored dry at 4 °C.

4.2.2 Chemicals and reagents

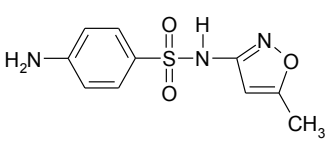
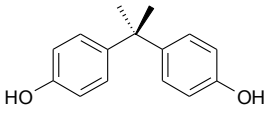
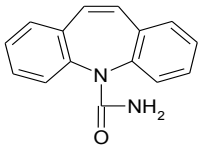
Three notable trace organic contaminants - namely sulfamethoxazole, bisphenol A, and carbamazepine - were selected for this study. These compounds have similar molecular weights and molecular dimensions (Table 4-1), and are frequently detected at trace level in raw and secondary treated sewage. However, their dissociation constants and intrinsic hydrophobicity (log KOW) differ markedly (Table 4-2). The compounds were purchased from Sigma-Aldrich (St. Louis, MO) and were reported to be of 98% purity or higher. Stock solutions (1 g/L) were prepared in pure methanol. They were stored at -18 ° C and used within one month.

Sigma-Aldrich humic acid (St. Louis, MO, USA) was selected as a model organic foulant in this study. This humic acid has been used in many previous membrane fouling investigations and its characteristics are well known (see for example Schäfer et al. (2006) and Tang et al. (2007). All other chemicals used in this study were of analytical grade.

4.2.3 Crossflow membrane filtration system

A laboratory-scale, crossflow membrane filtration test unit with a rectangular stainless steel crossflow cell was used in this study. This cell had an effective membrane area of 40 cm^2 (4 cm × 10 cm) with a channel height of 2 mm. The unit was equipped with a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN, USA) capable of providing pressures up to 6800 kPa and a flow rate of 4.2 L/min. The temperature of the test solution was kept constant using a chiller/heater (Neslab RTE 7, Newington, NH, USA) equipped with a stainless steel heat exchanger coil, which was submerged directly into a stainless steel reservoir. Permeate flow was measured by a digital flow meter (Optiflow 1000, Agilent Technologies, Palo Alto, CA, USA) connected to a PC, and the cross flow rate was monitored using a rotameter.

Table 4-1: Intrinsic physicochemical properties of the trace organic contaminants.

	Sulfamethoxazole	Bisphenol A	Carbamazepine
Molecular weight (g/mol)	253.3	228.0	236.3
Molecular width[a] (nm)	0.526	0.383	0.507
Molecular height[a] (nm)	0.587	0.587	0.529
Molecular length[a] (nm)	1.031	1.068	0.891
Log K_{OW} [b]	0.89	3.32	2.45
Dissociation constant[b]	pK_{a1} = 1.4, pK_{a2} = 5.8	pK_a = 10.1	pK_{a1} = -0.49, pK_{a2} = 13.94
Molecular structure			

[a] Reference source: Calculated using ChemOffice 2005.

[b] Reference source: SciFinder Scholar, data calculated using Advanced Chemistry Development (ACD/Labs) Software V8.14 for Solaris (1994-2007 ACD/Labs).

4.2.4 Experimental protocol

The membrane fouling/scaling and subsequent rejection experimental protocol was conducted in two distinctive phases. An organic fouling layer was allowed to develop on the membrane surface in the first phase. The membrane was compacted using Milli-Q water at 1800 kPa for at least 1 h until a stable baseline flux was obtained. A fouling layer was then allowed to develop using a foulant cocktail consisting of 20 mg/L of humic acid in a background electrolyte solution containing 20 mM NaCl, 1 mM $NaHCO_3$, and 1 mM $CaCl_2$. The volume of the feed water solution was 7 L. Following the addition of the foulants, the crossflow velocity and permeate flux were adjusted to be 30.4 cm/s and approximately 140 L m^{-2} h^{-1} (39 µm/s), respectively. This fouling development step was carried out for 20 h and the feed solution was kept at pH 8.

The second phase began immediately after the development of the organic fouling layer. An aliquot of individual trace organic contaminant was added to the feed reservoir to result in a concentration of 750 µg/L. The solution pH was raised to 11 by adding an appropriate volume of 1 M NaOH to induce $CaCO_3$ scaling. The permeate flux was readjusted to approximately 54 L m^{-2} h^{-1} (15 µm/s) while the crossflow velocity was maintained at 30.4 cm/s. Feed and permeate samples were collected at regular time intervals for analysis. All experiments were terminated when the permeate flux became stable again. In general, this scaling phase lasted about 24 h. Although membrane fouling and scaling were induced under rather unrealistic conditions in this study, this allows for a systematic investigation of the effects of membrane fouling and scaling on the rejection of trace organic contaminants.

To examine the rejection of trace organic contaminants under a range of permeate fluxes by the clean NF270 membrane, a similar protocol but without the fouling development step was adapted. Following a standard membrane compaction procedure, a feed solution containing only 20 mM NaCl, 1 mM $NaHCO_3$, and 750 µg/L of a selected trace organic contaminant was introduced to the feed reservoir. The feed solution pH was again kept constant at pH 11 by adding the necessary volume of 1 M NaOH. At each permeate flux, the system was stabilised for at least one hour before feed and permeate samples were collected for analysis.

In all experiments described above, the temperature of the experimental solution was kept constant at 20.0 ± 0.1° C. Both permeate and retentate were recirculated back to the feed reservoir throughout the entire experiment. Observed rejection is defined as $R = 100 \times (1 - C_P//C_F)$, where C_P and C_F are the permeate and the feed concentrations, respectively.

4.2.5 SEM-EDS analysis

The morphology and distribution of calcium deposited on the membrane surface were examined by scanning electron microscopy using a JEOL JSM-6460A instrument, with additional semi-quantitative energy dispersive spectrometer analysis. Prior to SEM analysis, the membrane samples were air-dried and subsequently coated with an ultra-thin layer of carbon. Extreme care was taken when preparing the fouled and scaled membrane samples to ensure that the fouling and scaling layer remained intact.

4.2.6 Analytical methods

A Shimadzu HPLC system (Shimadzu, Kyoto, Japan) equipped with a Supelco Drug Discovery® C-18 column (with diameter, length and pore size of 4.6 mm, 150 mm, and 5 µm, respectively) and a UV–Vis detector was used to measure the concentrations of the trace organic contaminants in the feed and permeate. The detection wavelength was set at 280 nm for all three trace organic contaminants selected in this study. The mobile phase used for gradient elution was Milli-Q-grade deionised water buffered with 25 mM KH_2PO_4 and acetonitrile, which was delivered at 1 mL/min through the column. Calibration generally yielded standard curves with coefficients of determination (R^2) greater than 0.98 within the range of experimental concentrations used. The analysis was carried out immediately upon the conclusion of each experiment. A sample injection volume of 50 µL was used, and the quantification limit for all the analytes under investigation using these conditions was approximately 20 µg/L.

4.3 Results and discussion

4.3.1 Membrane characteristics

The NF270 nanofiltration membrane selected for this study consists of an ultra-thin semi-aromatic piperazine-based polyamide layer on top of a polysulfone microporous support reinforced with a polyester non-woven backing layer (Freger et al. 2002). Mänttäri et al. (2004) provided a comprehensive characterisation of this membrane(Mänttäri et al. 2004). According to these authors, the NF270 membrane has several unique properties that make it a strong candidate for the treatment of high fouling potential wastewater (Mänttäri et al. 2004). In fact, data independently obtained in our study (Table 4-2) are in good agreement with the findings reported by Mänttäri et al. (2004). Because the polyamide layer that makes up the membrane active layer contains both carboxylic and amine functional groups that can ionise in an aqueous solution, the membrane surface zeta potential is highly negative at pH 4 or higher. Contact angle measurement of the membrane surface using the standard sessile drop technique indicates that the membrane is also very hydrophilic (Table 4-2). In addition, the NF270 has a very smooth surface with an average surface roughness of 8.6 nm (taken by atomic force microscopy measurement on a sample size of 2 µm by 2 µm). These unique set of membrane properties renders the NF270 membrane quite resistant to organic fouling (Mänttäri et al. 2004). It has also been

shown that the membrane responds very well to chemical cleaning under a relatively harsh condition (elevated pH and temperature) without any significant compromise in the membrane separation capacity (Mänttäri et al. 1997). Another important aspect of the NF270 membrane is the unusually high organic rejection-permeability characteristic.

Table 4-2: Properties of the membrane used in this study

Membrane	Pure water permeability ($Lm^{-2}h^{-1}bar^{-1}$)	Average pore diameter[a] (nm)	NaCl rejection (%)	Contact Angle (°)	Virgin membrane zeta potential[a] (mV)		
					pH 4	pH 6	pH 8
NF270	13.5	0.84	40.0	23.7	-8.0	-19.4	-24.7

[a] (Nghiem and Hawkes 2007)

Mänttäri et al. (2004) compared glucose rejection and permeate flux of the NF270 membrane to more than 10 other nanofiltration membranes and found that the NF270 had the second highest permeability with a glucose rejection value of over 90% (Mänttäri et al. 2004). The authors attributed this high rejection-permeability characteristic of the NF270 membrane to a high porosity of the membrane active layer and/or a very thin selective layer. Indeed, the membrane's average pore diameter has been estimated to be 0.84 nm (Nghiem et al. 2004) while the active layer thickness was reported to be approximately 20 nm (Freger et al. 2002). It is also noteworthy that the membrane has a relatively low salt rejection value making it a desirable membrane for wastewater treatment when desalination or hardness removal is not required. More importantly, as we reported in a previous study (Nghiem and Hawkes 2007), the magnitude of the influence of membrane fouling on trace organic contaminant rejection could be quite significant for loose NF membranes. Therefore, the NF270 membrane can be seen to be ideal to investigate the effect of multiple fouling/scaling layers on the rejection of trace organic contaminants.

4.3.2 Membrane fouling and scaling development

Permeate flux decline in response to membrane fouling differed quite distinctively from that to scaling. Excellent reproducibility was achieved with the accelerated membrane fouling and scaling development protocol used in this study. A typical permeate flux profile as a function of time during organic fouling and scaling development is presented

in Figure 4-1. Organic fouling-induced by the accelerated fouling protocol-resulted in an immediate and significant permeate flux decline within the first few hours of the experiment (Figure 4-1). The permeate flux became stable at approximately 15 µm/s after about 20 h. At the completion of the organic fouling development stage, in order to induce scaling, the feed solution pH was raised to 11. At pH 11, the carbonate balance was shifted towards the fully deprotonated species CO_3^{2-}. Consequently, the solubility limit of $CaCO_3$ was exceeded and the feed solution became supersaturated with respect to $CaCO_3$. At pH 11, the Langelier saturation index (LSI) of the feed solution tested in this study was calculated to be 2.5 for $CaCO_3$, clearly indicating a supersaturation condition.

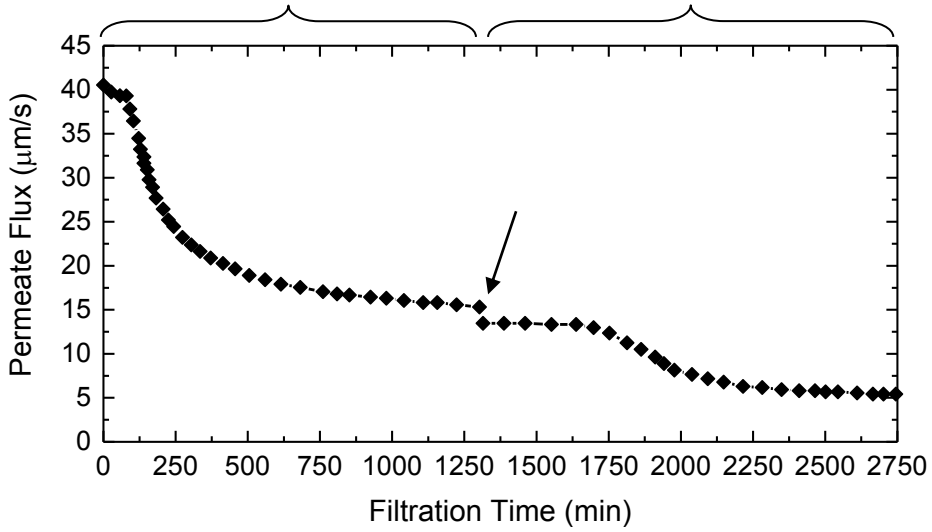


Figure 4-1: Permeate flux as a function of filtration time during organic fouling development followed by $CaCO_3$ scaling development. Feed solution: 20 mM NaCl, 1 mM $NaHCO_3$, 1 mM $CaCl_2$, and 20 mg/L of humic acid. The solution pH was 8 and 11 during fouling and scaling development, respectively.

The morphology of the scaling layer confirmed the deposition of calcium carbonate on the membrane surface (Figure 4-2A). Electron dispersive spectroscopy (EDS) analysis also confirmed the presence of calcium as the only dominant metallic ion in the scaling layer (Figure 4-3). In addition, EDS analysis of the scaled membrane resulted in a Ca:C:O atomic ratio of 1:1.6:2.6, which is very close to the atomic ratio of $CaCO_3$ of 1:1:3. Sulphur was not detected in the $CaCO_3$ scaling layer while a sulphur peak was clearly evident from the EDS

spectrum of the virgin membrane (Figure 4-3). This sulphur peak could possibly be attributed to the polysulphone supporting layer of the NF270 membrane.

The filtration behaviour reported in this study differs substantially from that of pure $CaCO_3$ scaling. It is striking to note that membrane scaling did not occur immediately upon the increase of the feed solution pH to 11. In fact, an induction period of approximately 400 min was observed prior to the onset of membrane scaling. Furthermore, membrane scaling following humic acid fouling did not result in a complete loss of permeate flux. In contrast, $CaCO_3$ scaling occurred immediately and led to a complete loss of flux in a filtration experiment conducted under the same experimental conditions but in the absence of humic acid (data not shown). This is consistent with the morphology of the $CaCO_3$ scaling layer as shown in Figure 4-2B. In the absence of humic acid, the $CaCO_3$ crystals are much larger than those in the presence of humic acid (Figure 4-2A). The complete loss of permeate flux can also be attributed to the agglomeration of $CaCO_3$ crystals in the absence of humic acid (Figure 4-2B).

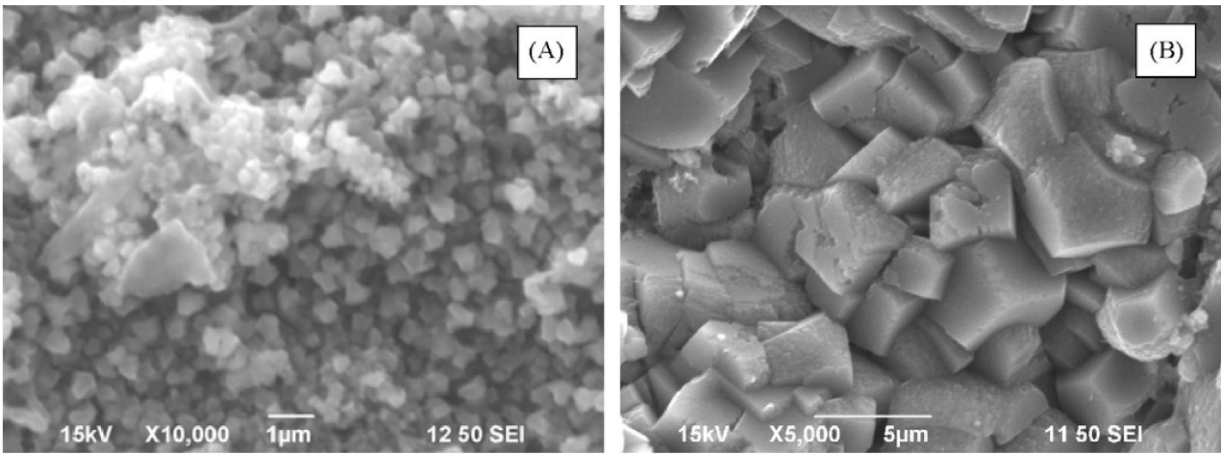


Figure 4-2: SEM picture of the NF270 membrane surface: (A) $CaCO_3$ scaling following humic acid fouling and (B) $CaCO_3$ scaling in the absence of humic acid.

It should be noted that supersaturation does not necessarily lead to immediate precipitation (Sheikholeslami 2003). In good agreement with the data reported here, a prolonged induction period preceding the spontaneous formation of calcite in the presence of humic substances was observed by Klepetsanis et al. (2000). In addition, a significant change to the rate of calcite crystal growth occurred when humic substances were added to metastable supersaturated calcium carbonate solutions (Amjad et al. 1998, Hoch et al. 2000). The influence of humic acid on $CaCO_3$ crystal growth is also evident in the current study.

While $CaCO_3$ crystals are clearly visible in Figure 4-2A, these crystals are small and quite uniform in size. The crystals appear to be loosely packed which can possibly explain the permeable nature of the scaling layer observed here. It is noted that at the end of the scaling development stage, the permeate flux was stable at 5 µm/s. In contrast, it is well known that in a pure solution, calcium carbonate can form a dense and adherent scaling layer with large sized calcite crystals, which results in a complete loss of permeate flux (Tzotzi et al. 2007).

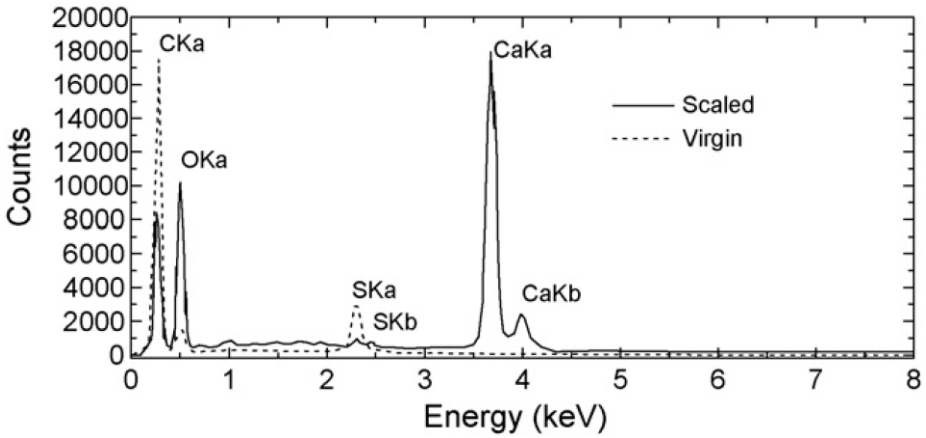


Figure 4-3: EDS spectrum of the NF270 membrane surface under clean and prefouled/scaled conditions.

Humic acid fouling followed by $CaCO_3$ scaling was simulated using an accelerated protocol in this study. Nevertheless, results reported here have an obvious practical implication. Due to the complexity of secondary treated effluent or surface water, it is likely that membrane fouling will precede inorganic scaling (Xu et al. 2010, Yang et al. 2008). The interplay between organic fouling and inorganic scaling may have a profound impact on the rejection of trace organic contaminants as will be described in the next section.

4.3.3 Effects of fouling/scaling on the membrane rejection behaviour

Solute rejection values were monitored during the scaling development phase to elucidate the influence of membrane scaling on the separation behaviour of the NF270 membrane. Rejection values of both inorganic salts (measured by conductivity) as well as trace organic contaminants were stable during the scaling induction period of approximately 400 min (Figure 4-4 to 4-6). However, at the onset of $CaCO_3$ precipitation on the membrane surface, inorganic scaling resulted in a marked decrease in the rejection of all three

trace organic contaminants. Due to membrane scaling, the rejection values of sulfamethoxazole, bisphenol A and carbamazepine were reduced by 60%, 43%, and 70%, respectively. The impact of membrane scaling on the rejection of trace organics was much more severe than that due to organic fouling as previously reported (Nghiem and Hawkes 2009, Verliefde et al. 2009). At the onset of membrane scaling, the decrease in trace organic rejection mirrors the decrease in permeate flux. Nevertheless, the influence of membrane scaling on conductivity was significantly less than on the rejection of trace organic contaminants (Figure 4-4).

The decrease in solute rejection can partially be attributed to the decrease in permeate flux. Due to membrane scaling, it is noteworthy that the permeate flux decreased from 15 µm/s to approximately 5 µm/s. In fact, the influence of permeate flux on solute rejection can be quantitatively modelled for a membrane of known effective pore size (Nghiem et al. 2004). Figure 4-7 shows the rejection of both trace organic contaminants and conductivity as a function of the permeate flux under clean membrane conditions (i.e. without any interference of organic fouling or scaling). Without the interference of membrane fouling and scaling, conductivity rejection decreased by approximately 20% as the permeate flux decreases from 16 µm/s to 4 µm/s. The decrease in the rejection of all three trace organic contaminants was substantially less. Therefore, it is clear that permeate flux decline is not a major cause of the significant decrease in trace organic rejection observed in this study.

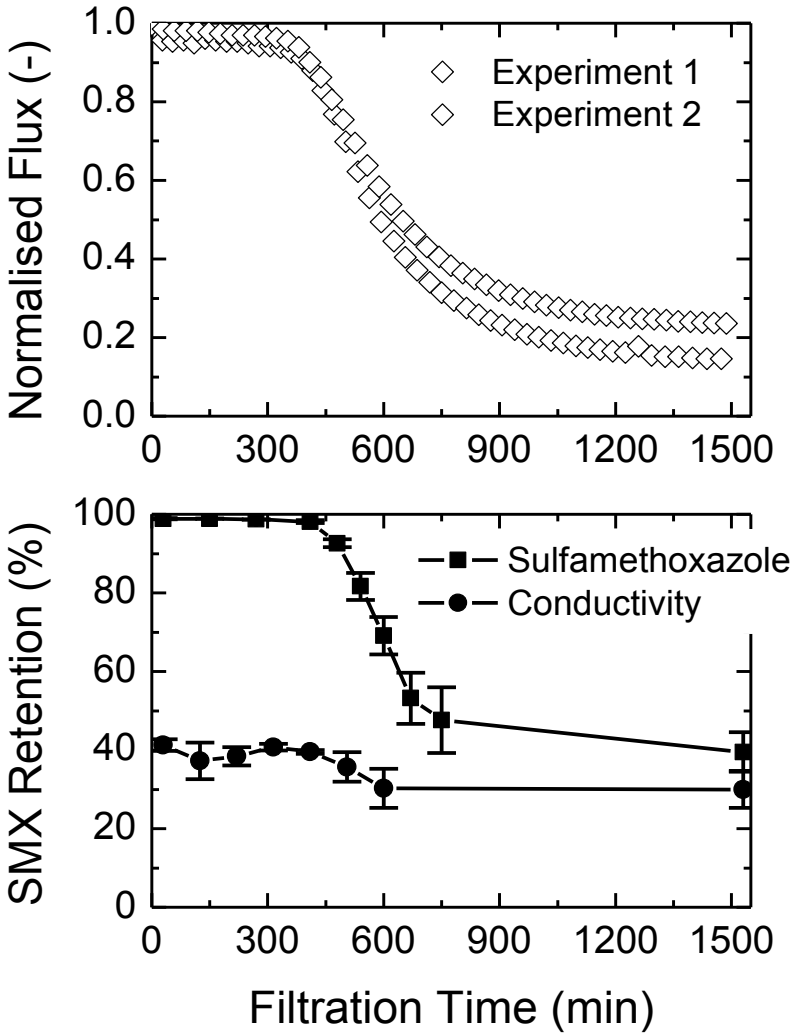


Figure 4-4: Effects of $CaCO_3$ scaling on the permeate flux and rejection of sulfamethoxazole and conductivity. Only the scaling development stage was depicted. Feed solution composition is as in Figure 4-1. Error bar shows standard deviation of repetitive experiments.

The influence of membrane fouling/scaling on solute rejection can be governed by three major mechanisms. For large pore size membranes, fouling/scaling can result in pore constriction, which can ultimately lead to an increase in rejection of some solutes. The fouling or scaling layer deposited on the membrane surface can also modify the membrane surface charge density, altering the separation of charged solutes. Another important mechanism suggested by Elimelech and co-workers (Hoek and Elimelech 2003, Lee et al. 2005, Ng and Elimelech 2004) is the hindrance of solute diffusion from the vicinity of the membrane surface back to the bulk solution due to the presence of a porous cake layer, result-

ing in the so-called cake-enhanced concentration polarisation effect. Cake-enhanced concentration polarisation can lead to a higher concentration of solute at the membrane surface. Because the intrinsic rejection of the membrane remains unchanged, cake-enhanced concentration polarisation can eventually lead to a higher solute concentration in the permeate, or in other words, a decrease in rejection.

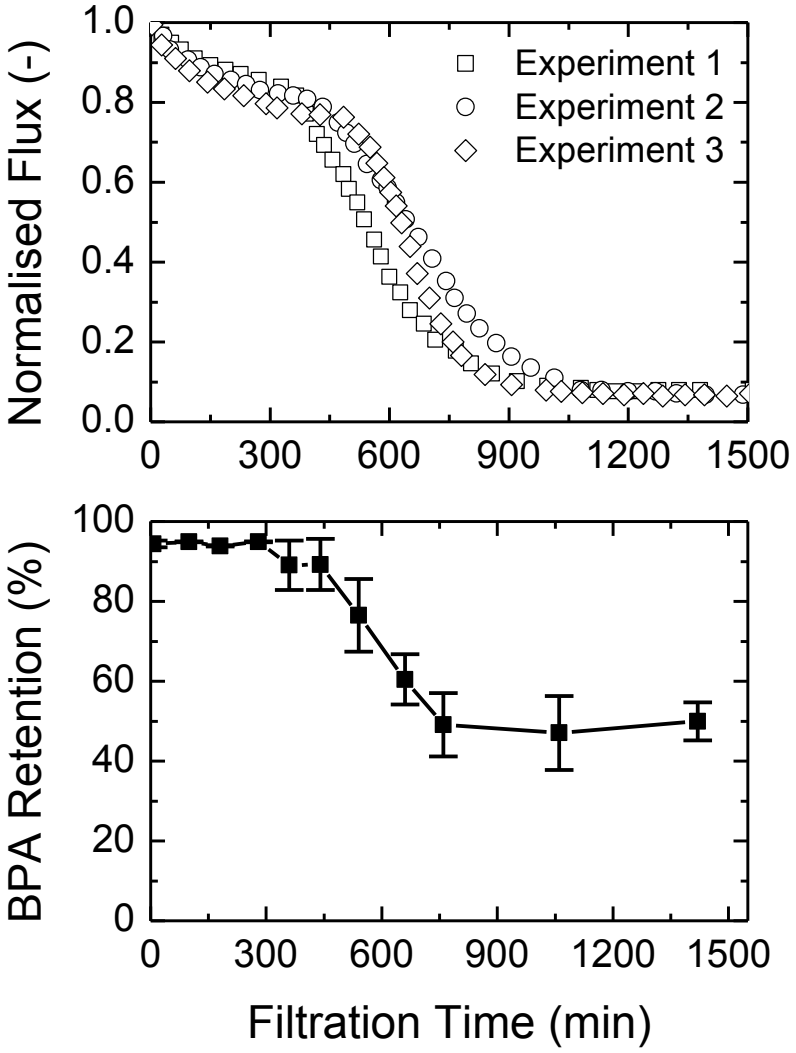


Figure 4-5: Effects of $CaCO_3$ scaling on the permeate flux and rejection of bisphenol A. Only the scaling development stage was depicted. Feed solution composition is as in Figure 4-1. Error bar shows standard deviation of repetitive experiments.

It is clear that pore constriction cannot explain the consistent decrease in solute rejection as a result of membrane scaling reported in this study. Alteration of the membrane surface charge density can influence the rejection of charged solutes. However, carbamazepine is a neutral compound under the experimental conditions used in this study. Given

the significant reduction of carbamazepine rejection of almost 70% due to membrane scaling, membrane surface charge modification is probably not a major mechanism governing the influence of membrane scaling on the rejection of trace organic contaminants. In addition, the reductions in rejection of both sulfamethoxazole and bisphenol A are not as severe as that of carbamazepine. This can be attributed to the fact that electrostatic interactions between the negatively charged membrane and the negatively charged sulfamethoxazole or bisphenol A remain quite prevalent. Therefore, it can be concluded that cake-enhanced concentration polarisation is responsible for the rapid decline in rejection of the three trace organic contaminants reported here. In fact, decrease in rejection of trace organic contaminants due to cake-enhanced concentration polarisation following membrane fouling has been widely reported in the literature. Organic fouling results in a relatively small cake-enhanced concentration polarisation effect, which can lead to a small but nevertheless discernible decrease in the rejection of trace organic contaminants. On the other hand, colloidal fouling can produce a porous cake layer, resulting in a strong cake-enhanced concentration polarisation effect. Consequently, colloidal fouling can lead to a more severe decrease in the rejection of trace organic contaminants as compared to organic fouling (Lee et al. 2005, Nghiem et al. 2008, Verliefde et al. 2009). Previous studies have also demonstrated that the impact of cake-enhanced concentration polarisation on rejection can be influenced by the relative size of the membrane pores and the size of the solute. Ng and Elimelech (2004) reported that the decrease in the rejection of ethylene glycol and glycerol by the reverse osmosis LFC-1 membrane due to silica colloidal fouling was 33% and 25%, respectively (under the most severe cake-enhanced concentration polarisation). The molecular weight of ethylene glycol and glycerol is 62.1 g/mol and 92.1 g/mol, respectively. In good agreement with the current study, the effect on NaCl rejection was considerably less than that on these two organic compounds. In contrast, Ng and Elimelech (2004) reported that the silica colloidal cake layer showed negligible effect on the rejection of larger organic compounds such as xylose (molecular weight of 150.1 g/mol).

The NF270 membrane used in this study is a loose nanofiltration membrane with an effective pore size larger than the molecular size of the three trace organic contaminants (Tables 4-1 and 4-2). Considerable influence of organic and silica colloidal fouling on the rejection of sulfamethoxazole by the NF270 membrane has been reported (Lee et al. 2005, Ng and Elimelech 2004, Nghiem et al. 2008, Verliefde et al. 2009, Xu et al. 2006a). However, the reduction in trace organic rejection due to the combination of humic acid fouling and $CaCO_3$ scaling reported here was much more dramatic than that previously reported in

the literature with respect to organic and colloidal fouling (Ng and Elimelech 2004, Nghiem et al. 2008, Verliefde et al. 2009, Yangali-Quintanilla et al. 2009). It is clear that the observed cake-enhanced concentration polarisation phenomenon was more severe than that reported with colloidal and organic fouling.

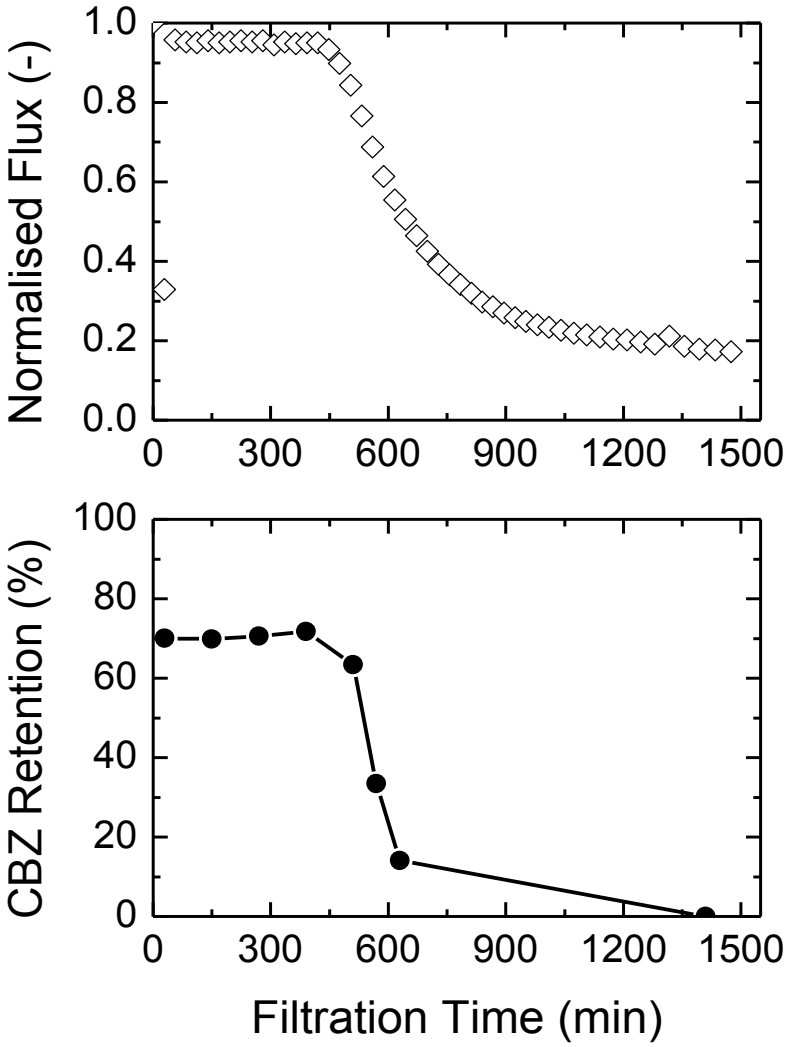


Figure 4-6: Effects of $CaCO_3$ scaling on the permeate flux and rejection of carbamazepine. Only the scaling development stage was depicted. Feed solution composition is as in Figure 4-1.

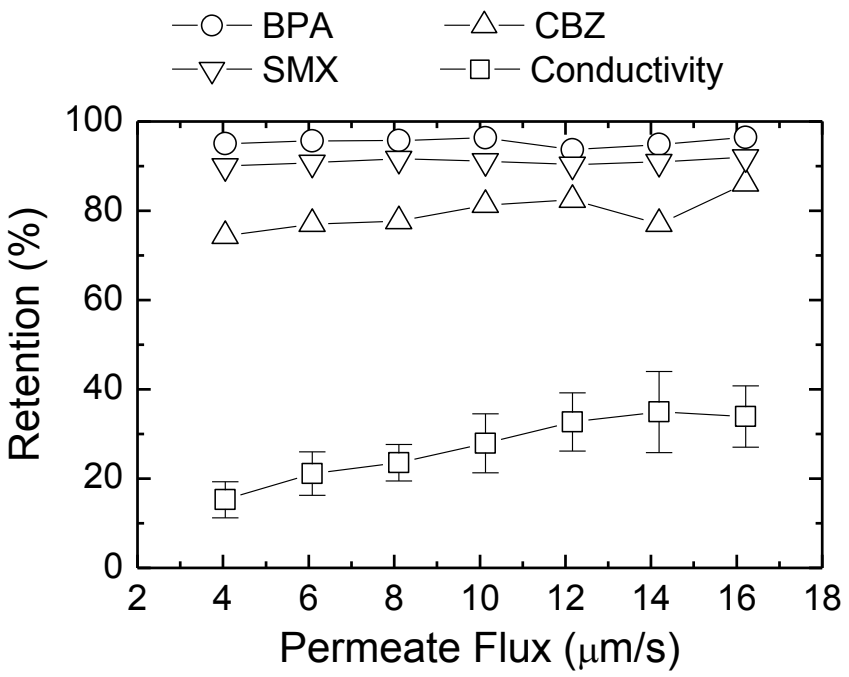


Figure 4-7: Effects of permeate flux on the rejection of sulfamethoxazole, bisphenol A, carbamazepine, and conductivity under clean membrane conditions. Feed solution: 20 mM NaCl, 1 mM $NaHCO_3$, 1 mM $CaCl_2$ pH = 8. Error bar shows standard deviation of 3 repetitive experiments.

4.3.4 Cake-enhanced concentration polarisation

In this study, a combination of humic acid fouling followed by $CaCO_3$ scaling was examined to elucidate the impact of cake-enhanced concentration polarisation on solute rejection. Humic acid fouling by itself may not result in a substantial cake-enhanced concentration polarisation effect as previously reported in the literature. However, as discussed above, humic acid can significantly influence the morphology of the $CaCO_3$ crystals, resulting in a rather porous scaling layer. Such a scaling layer can induce a strong cake-enhanced concentration polarisation effect similar to that of colloidal fouling previously reported by several researchers. More importantly, the combination of humic acid fouling and $CaCO_3$ scaling could result in the so-called 'extended cake-enhanced concentration polarisation' effect, which can be schematically described in Figure 4-8. Since the $CaCO_3$ scaling layer was formed on top of the humic acid fouling layer, the wall shear rate at the membrane between the scaling layer and the membrane surface will be dramatically reduced. Wall shear rate is an important factor governing the extent of cake-enhanced concentration polarisation effect. Ng and Elimelech (2004) reported that the rate of decline in solute

rejection due to cake-enhanced concentration polarisation correlated inversely with wall shear rate. As a result, the low wall shear rate as a consequence of combined humic acid fouling and $CaCO_3$ scaling can possibly account for the dramatic decrease in the rejection of trace organic contaminants reported here.

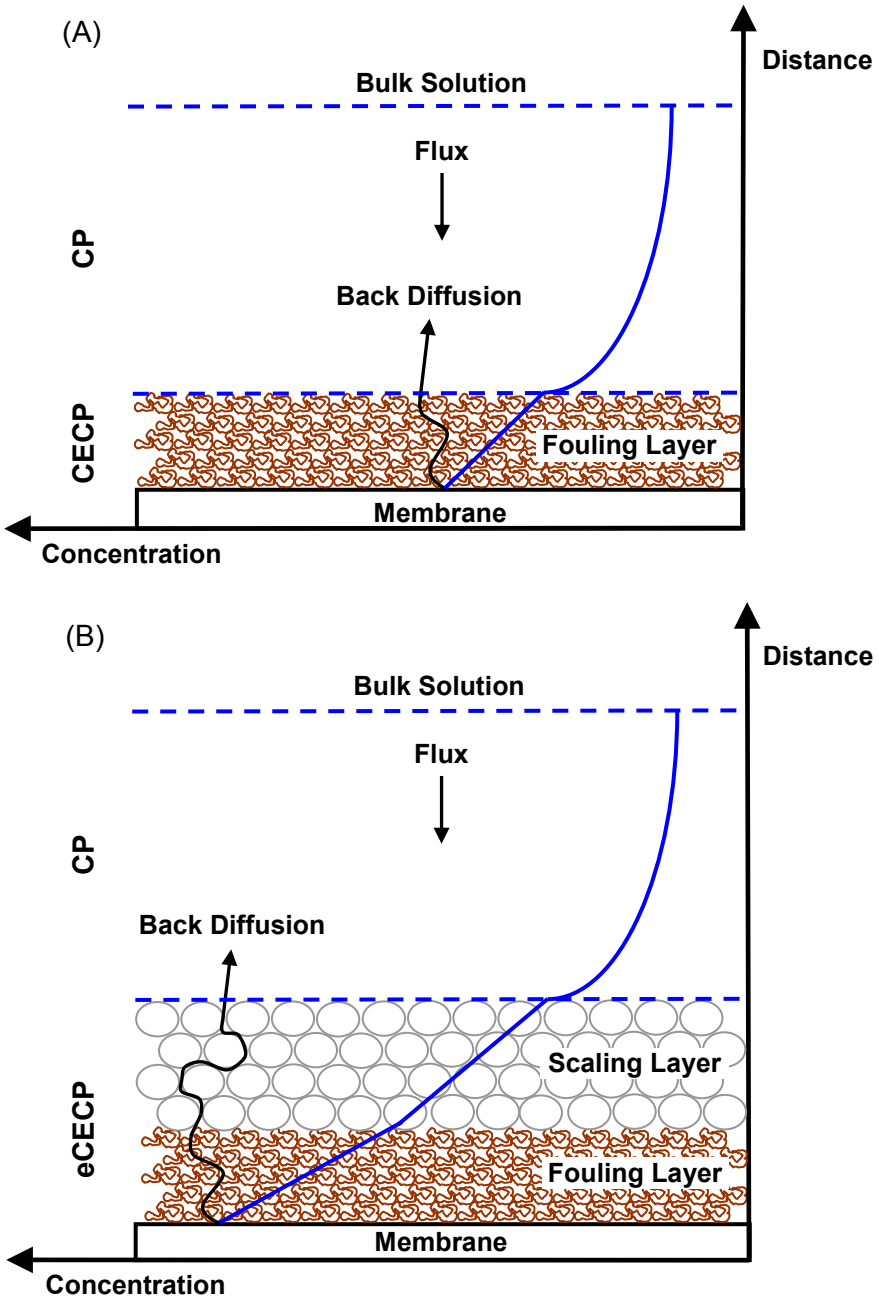


Figure 4-8: Schematic diagram of the cake-enhanced concentration polarisation phenomenon: (A) cake-enhanced concentration polarisation caused by a single fouling layer and (B) the proposed extended cake-enhanced concentration polarisation phenomenon caused by a combination of membrane fouling and scaling.

4.4 Conclusions

Results reported here indicate that $CaCO_3$ scaling on top of a humic acid fouling layer does not necessarily lead to an immediate and complete loss of permeate flux but can result in a severe impact on the rejection of trace organic contaminants. Due to the presence of humic acid in the feed solution, $CaCO_3$ scaling on top of an organic fouling layer can differ substantially from that of a pure $CaCO_3$ solution. A prolonged induction period was consistently observed prior to the onset of membrane scaling. SEM analysis also confirmed the absence of any large $CaCO_3$ crystals. In fact, the $CaCO_3$ crystals on the membrane surface were quite small and similar in size, which would result in a relatively porous cake layer. At the onset of $CaCO_3$ scaling, the rejection of all three trace organic contaminants investigated here started to decrease dramatically. The decrease in rejection reported here was much more severe than what had been previously observed with a single layer of either organic or colloidal fouling. Such severe decrease in rejection can be attributed to the extended cake-enhanced concentration polarisation effect that occurred as a result of the combination of membrane fouling and scaling. The porous $CaCO_3$ scaling layer could cause a substantial cake-enhanced concentration polarisation effect. In addition, the top $CaCO_3$ scaling layer could reduce the wall shear rate within the underlying humic acid fouling layer, resulting in an additional concentration polarisation effect.

5 Summary and conclusions

Nanofiltration/reverse osmosis (NF/RO) processes may be a suitable means for the treatment of landfill leachate and municipal wastewater prior to discharge into surface waters as well as wastewater reclamation schemes, respectively. Out of the large number of impact factors on the rejection of trace organic contaminants (TrOCs) by NF/RO, membrane fouling was selected to study its impact on the removal of TrOCs from synthetic wastewater by nanofiltration. This topic was chosen, because even a very comprehensive pre-treatment of wastewater may not be able to eliminate fouling causing constituents entirely. Consequently, membrane fouling, particularly organic fouling, has always been and will be an inseparable part of membrane filtration processes using feed water polluted with e.g. organic macromolecules. In addition to organic and inorganic fouling, the impact of the presence or absence of divalent ions, namely Ca^{2+} was studied, since the importance of this common wastewater constituent on membrane fouling has been shown in previous research.

In chapter 2 the impact of varying concentrations of calcium in the feed water on development and implications of organic membrane fouling by humic acid was studied for the commercially available NF270 membrane. The results reported demonstrate a considerable effect of the feed water calcium concentration on membrane fouling, which is consistent with several previous studies. The observed increase of fouling due to the presence of calcium in the feed was attributed to intermolecular bridging between the organic foulant and the membrane (solute-membrane interaction) caused by cations. Furthermore, complexation between calcium and the functional groups of the humic acid (solute-solute interaction) may occur leading to a reduced interchain repulsion between the macromolecules of the humic acid. This results in the formation of small and coiled macromolecules. Additionally, calcium can partly neutralise the membrane charge (solute-membrane interaction).

The fouling observed for a feed solution containing humic acid and calcium (0.5 and 1 mM) occurred in two distinctive steps, an initial steep decrease, which was attributed to pore blocking, followed by a more gradual decline, interpreted to be due to a second fouling mechanism, namely the formation and compaction of the cake layer on the membrane surface. The overall extent of flux decline with time was clearly dependent on the calcium concentration. There appears to be a critical calcium concentration of 0.5 mM, at which, under the conditions of this study, fouling was most severe. In contrast, both the absence of calcium as well as a higher concentration (4 mM) of calcium caused fouling to

a lower extent. It is hypothesised that a high calcium concentration may lead to the formation of large and compact aggregates (or flocs) that are bigger than the pores and therefore cannot penetrate into the pores. At lower calcium concentrations smaller aggregates are formed, resulting in a dense cake layer and/or pore blocking.

The study also showed a significant influence of fouling on the rejection of bisphenol A (BPA). An initial drop of the BPA rejection was observed for all calcium concentrations studied. Depending on the calcium concentration, the extent of the drop differed significantly leading to a large variation of the extent of BPA rejection. Adsorption of BPA to the membrane surface and possibly the humic acid appears to be responsible for the high rejection in the beginning of the test which would be consistent with previous studies where a significant adsorption of hydrophobic, neutral compounds onto NF membranes was found. For the lowest fouling observed (at 0 mM of calcium), the BPA rejection was also the lowest of the study. This is attributed to limited pore blocking occurring in the absence of calcium resulting in a less dense fouling layer. At a calcium concentration of 4 mM large aggregates are hypothesised to be formed that are too large to block pores and also form a fairly porous cake layer on the membrane surface. Therefore, an additional mechanism, the so-called cake-enhanced concentration polarisation may also have been effective. That would have led to a decreased back diffusion of solutes into the bulk solution and hence a higher solute concentration near the membrane, which eventually results in a lower rejection.

Rejection increased commensurately with the extent of fouling. However, the highest rejection (at 1 mM of calcium) was not observed when fouling was most severe (at 0.5 mM of calcium). It is hypothesised that at 0.5 and 1 mM of calcium small coiled macromolecules are formed resulting in pore blocking and therefore leading to an enhanced sieving effect. Furthermore, the formation of a dense cake layer may have contributed to this additional sieving effect leading to an increase in rejection. However, a different transport mechanism of solutes due to hydrophobic interaction may explain the observation that at 1 mM of calcium the highest BPA rejection did not coincide with the most severe fouling. Due to the formation of a hydrophobic membrane fouling layer interactions of solutes with the membrane may be hindered, which could result in less solute partitioning and diffusion across the membrane. This has been reported as a major transport mechanism for hydrophobic solutes. All the mechanisms described may occur simultaneously and their single effects cannot easily be separated.

In chapter 3 the impact of calcium on organic membrane fouling and its implications on the rejection behaviour of the TrOC BPA is described. However, the focus of the study was expanded by an additional variation of the membrane physico-chemical properties (e.g. pore size, hydrophobicity, surface roughness) through inclusion of two more membranes in the work. Results demonstrate a considerable impact of the feed water calcium concentration on membrane fouling for the NF90 and TFC-SR2 membranes too. This is in accordance with the results for the NF270 membrane (chapter 2). Furthermore, similar phenomena were observed for the NF90 and TFC-SR2 as for the NF270, e.g. the occurrence of a critical calcium concentration at approximately 0.5 to 1 mM of calcium, where fouling and, hence, flux decline were most severe. Less fouling was again observed in case of the absence of calcium and a high concentration (4 mM) of calcium in the feed.

A clear impact of humic acid fouling in the presence of calcium in the feed solution on the membrane hydrophobicity, an important membrane characteristic, was observed for all three membranes tested. It was shown that membrane hydrophobicity for the fouled membranes is primarily governed by the adhesion of the humic acid layer irrespective of the initial surface characteristics of the clean membrane. The existence of a hydrophobic fouling layer on the membrane surface may potentially affect the separation process, particularly for hydrophobic compounds such as BPA.

As discussed above, an initial adsorption of BPA to the membrane was observed for all three membranes before the BPA concentration in the permeate reached a constant level. Similar to the NF270 membrane there was a considerable variation to the BPA rejection as a function of the extent of fouling also for the TFC-SR2 membrane. There are several antagonistic mechanisms governing BPA rejection such as pore blocking, cake-enhanced concentration polarisation and the impact of the fouling layer on hydrophobic solute-membrane interaction. This leads to a rather complex system of transport mechanisms. For the loose TFC-SR2 membrane, pore blocking or even pore plugging due to organic fouling resulted in a significant increase of BPA rejection for all calcium concentrations and in the absence of calcium. The BPA rejection correlated well with the extent of fouling. Cake enhanced concentration polarisation would have played a very minor role for the TFC-SR2 due to its relatively large pore size.

For the tight NF90 membrane, a small but still discernible increase of the BPA rejection under fouled conditions can be observed. Due to the average pore size of the membrane in the range of the molecular dimensions of BPA or even smaller, pore blocking would have played only a limited role in BPA rejection. The presence of a separating fouling layer

on the membrane surface is assumed to hinder interactions between the membrane and the solute (BPA) to a greater extent. This would result in less partitioning and diffusion across the membrane and therefore an increase in rejection.

The combined organic and inorganic fouling (scaling) and the resulting implications on rejection of three selected TrOCs by the NF270 membrane are discussed in chapter 4. Results reported indicate that $CaCO_3$ scaling on top of a humic acid fouling layer does not necessarily lead to an immediate and complete loss of permeate flux. In contrast, 'pure' $CaCO_3$ scaling occurred immediately and led to a complete loss of flux when humic acid was absent in the feed. Scanning electron microscopy analysis confirmed differences in the nature of the scaling layer in the presence or absence of humic acid, an observation which is consistent with the observed filtration behaviour. In the presence of humic acid $CaCO_3$ crystals appear to be small and rather loosely packed which could explain the permeable nature of the scaling layer and the resulting prevention of a complete loss of flux. Furthermore, the observed prolonged induction period prior to the onset of scaling is in good agreement with scaling studies on solutions containing humic substances reported in the literature. On the other hand, in the absence of humic acid large sized $CaCO_3$ crystals are formed that tend to agglomerate and form a dense and adherent scaling layer on top of the membrane surface.

Monitoring of the membrane performance during the stage of scaling development showed a dramatic decrease of the rejection of all three trace organic contaminants starting right at the onset of $CaCO_3$ scaling. The decrease in rejection of 45, 60 and 70% for bisphenol A, sulfamethoxazole, and carbamazepine, respectively, was much more extensive than what had been previously observed with a single layer of either organic or colloidal fouling. The observed flux decline could be ruled out as a major cause of the significant decrease in trace organics rejection observed in this study. In general, there are three major mechanisms responsible for solute rejection under fouling/scaling conditions, namely pore constriction/blocking, modification of the membrane surface charge, and cake-enhanced concentration polarisation. Firstly, the observed consistent decrease in solute rejection for all TrOCs tested cannot be attributed to pore constriction/blocking. Also, alteration of the membrane surface charge density cannot explain the severe drop of rejection for carbamazepine since it is a neutral compound at the conditions used in the study. However, for the negatively charged solutes sulfamethoxazole and BPA this mechanism would be expected to have played a role in governing rejection.

It is concluded that cake-enhanced concentration polarisation has caused the rapid decline in rejection of the three TrOCs tested here. This transport mechanism has been reported in the literature to be relatively weak for organic fouling and strong for colloidal fouling. However, the combination of organic fouling and $CaCO_3$ scaling could result in the so-called 'extended cake-enhanced concentration polarisation effect'. The porous $CaCO_3$ scaling layer could cause a substantial cake-enhanced concentration polarisation effect. In addition, the top $CaCO_3$ scaling layer could reduce the wall shear rate within the underlying humic acid fouling layer, resulting in an additional concentration polarisation effect.

It has been shown that fouling (organic fouling, combined organic/inorganic fouling, fouling in the presence of calcium) may have a considerable impact on the removal of TrOCs by nanofiltration membranes. Although fouling can improve the rejection of TrOCs under certain conditions, measures should be taken to generally avoid fouling since it also negatively affects the membrane performance (flux) and membrane lifetime. There are several parameters in NF/RO membrane filtration systems that should be addressed in order to mitigate fouling such as the membrane (module) design, pre-treatment of the feed stream, and operational aspects (e.g. recovery, use of anti-biofouling agents and anti-scalants). Designing tailor-made membranes (e.g. by interfacial or grafting polymerisation, incorporation of nanoparticles) aims at higher selectivity, rejection tendency and low fouling propensity. Thereby, membranes with characteristics adjusted to the conditions of the intended application may be developed. Another important aspect is the pre-treatment of the feed. There are probably only few applications, which are suitable for a stand-alone operation of a NF/RO membrane system. Most (environmental) applications such as drinking water treatment or wastewater reclamation/reuse will need an appropriate pre-treatment like microfiltration, ultrafiltration, membrane bioreactors or even advanced oxidation processes (e.g. pre-ozonation). In terms of the operational parameters a suitable balance between the main objectives of meeting the product water (permeate) quality requirements, economical aspects like low energy consumption, and low fouling propensity must be found.

As a consequence of the complexity of the matter, as elaborated in this work, an expert engineering approach will be needed to work out the best solution for a particular task. Future developments in the membrane field will probably expand the scope of potential applications of this technology, but solutions will be more and more specific rather than following a general approach. In order to be able to set up a purpose-specific membrane

system the intrinsic mechanisms of the transport and the separation processes including, for example membrane fouling, need to be understood and considered in the design.

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